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METHODS OF STATISTICAL MECHANICS.*

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LECTURE I.—THE METHODS OF STATISTICAL MECHANICS.†

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(1) *Introduction.*—I wish to tell you how much I appreciate the pleasure and honor of addressing this Institute. Benjamin Franklin was the chief of my boyhood heroes. I was born only a few miles from his birthplace, and in my earliest years I held great notions of becoming a printer, which, however, did not progress beyond inferior work on a small hand press.

At a later time I became an admirer of that philosopher's shrewd wisdom and homely sayings; and I have never ceased to remain such. I continue to investigate the price of my whistles, seek to achieve that sensible humility which stoops to avoid bumps on the head, and have a strong conviction that leisure is indeed the *only* time in which a man can do things that are *fundamentally* interesting or useful.

I have often envied Franklin the simple and heroic age in which he lived. What a man! Printer, inventor, philosopher,

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statesman, diplomat, and with no lack of interest in the pleasures of more common men, he still found time to be a scientist of parts. Such careers are no longer possible. Science has become too hard and complicated. Kites and twine will no longer suffice to bring new fire from the skies. Some few gifted physicists can do a great deal with a lump of wax and some bits of glass, but most of us need all the facilities that an elaborate shop can provide and in addition have to struggle with a necessary but formidable elaboration of mathematical technique undreamt of by Franklin.

In the three lectures which I am to give, I am going to describe some of the methods and results of the science of statistical mechanics, a difficult and intricate, but nevertheless essential, branch of mathematical physics, whose development was not even commenced until many years after Franklin's death.

In the case of very complicated systems such as those studied by the chemist and biologist, it is very difficult, if not impossible, either to observe experimentally or predict theoretically the *precise* behavior of all the elements of any given system. Even if the chemist were told at a certain instant the exact locations, orientations, and velocities of all the atoms and molecules of which a reacting mixture is composed, and given the precise laws governing their individual behavior, the complexities of calculation would prevent him from predicting, even a fraction of a second later, the positions and chemical combinations of these elements. And for the biologist with his even more complicated systems, which consist not of a single reacting mixture but of an integrated combination of reaction zones, with an interplay between them of the physical-chemical processes taking place therein, the problem would be even more impossible of solution.

Nevertheless, in spite of the impossibility of precise observation and prediction, the chemist and the biologist have not been deterred from their labors. Even if they cannot follow, nor predict, the *exact* behavior of individual elements, they can observe and predict with remarkable surety the gross behavior of their systems as a whole. Each time that the chemist touches a match to a soap-bubble full of hydrogen and oxygen, he obtains an explosion; each time the bacteriologist autoclaves his glassware he kills the bacteria therein; and each time there is a war, I am afraid that the sociologist can predict that rich men will

profiteer and poor men die. These complicated phenomena do not lie beyond the realm of law and predictability.

To investigate the laws that do describe the gross behavior of systems containing many molecules, the science of *statistical mechanics* has been specially devised. The essence of its method consists in abandoning the attempt to predict the exact behavior of each molecule of a given system, and in determining rather by statistical methods what, on the average, will be the behavior of a great number of systems of similar constitution to the one of interest. The appeal thus made to the methods of statistics in the realm of physical chemistry is hence quite similar to the use of statistics in the biological sciences. More and more the chemist must turn to the methods of statistical mechanics in order to continue the theoretical development of his science, since he always deals with such a complicated collection of atoms that other methods are hard to apply.

(2) *Comparison of the Methods of Ordinary and Statistical Mechanics.*—A better idea of the methods of statistical mechanics will be obtained if we compare them first with those of ordinary mechanics and then with those of thermodynamics.

To take a concrete illustration, let us consider a gas composed of a large number of similar molecules moving about in all directions inside the walls of a container. And for simplicity let us take the molecules as small rigid elastic spheres.

To apply the methods of *ordinary mechanics* to such a gas, we should have to know at some given instant the positions and velocities of all the molecules. We could then foresee the collisions that were about to take place among the molecules themselves and between the molecules and walls of the container, and by applying the principles of the conservation of energy and momentum to these collisions could predict their result. We should thus, theoretically, be able to follow the further behavior of the gas and predict its condition at any future time. Practically, however, we should be lost in our calculations before the lapse of a thousandth of a second.

The difficulty of thus using the methods indicated by ordinary mechanics led in the older kinetic theory of gases to the introduction of various artificial simplifications, which are not now necessary, such as the assumption that all the molecules had the same velocity distributed in random directions, thus neglecting the

effect of collisions between the molecules themselves in changing the velocity. With the help of such simplifications, the methods of ordinary mechanics can lead to a number of valuable approximate results.

To apply the methods of *statistical mechanics* to determine the behavior of a gas, such as we have just postulated, we do not try to investigate the behavior of a single sample of the gas. Instead we consider an infinite number, or *ensemble*, of samples of the gas, started off with their molecules having all possible combinations of positions and velocities. Even though we cannot predict the precise behavior of any single sample of the gas, nevertheless, surprising as it may seem, we are able by the application of the principles of mechanics to obtain information as to the *statistical behavior* of the whole ensemble, and thus to draw conclusions as to the *probable* behavior of a single sample. Thus, for example, we find that of all the samples in the ensemble only an infinitesimal fraction of them will have the velocities of their molecules distributed in a manner appreciably different from that given by the Maxwell distribution law, and hence conclude that any given sample of gas will probably have the Maxwell distribution of velocities, and if displaced therefrom will tend to assume that distribution of velocities when left to itself.

At first sight it may seem surprising that the indicated method should be so powerful. A single sample of the gas with its many molecules was so complicated a system that we could not directly predict its future behavior, and yet by going to the much more complicated system of an infinite ensemble of similar samples we appear to obtain such predictions as to behavior. The apparent paradox, however, is dependent on the circumstance that in the first case with the single sample we attempted to predict the *actual* behavior of this single sample; with our new method, on the other hand, we content ourselves with a determination of the *statistical* behavior of the ensemble, and hence a prediction as to the *probable* behavior of a single sample.

A similar situation arises in the biological sciences. Thus a given man between the ages of thirty-four and thirty-five is such a complicated system of atoms and molecules that it is impossible to predict whether or not he will die within the coming year. Nevertheless, in a given country we have very reliable statistics as to the number of men per thousand between the ages of thirty-

four and thirty-five that die per annum, and hence we can make a very satisfactory prediction as to the probability or not that the man in question will live throughout the year. In this biological case the prediction is based on statistical laws obtained as a result of observations, while in the physical-chemical cases which will be of interest to us, the statistical laws are obtained as the result of deduction from the laws of mechanics. Nevertheless, the reason for the appeal to statistical methods is the same in both cases, the complexity of the systems making the use of more direct methods difficult.

The impression, of course, must not be gained that statistical mechanics can be profitably applied only to systems which are too complicated to permit the application of ordinary mechanical methods. Also in the case of a system of only a few degrees of freedom governed by simple equations of motion, we can consider an ensemble of such systems and discuss the statistical behavior of this ensemble, as has been particularly emphasized by Prof. E. B. Wilson.[1] An application of this kind can be of importance in case the initial values of the coördinates and velocities of the system at some given instant are unknown or not of interest. Nevertheless, for the most part, the chief driving force in the actual development of statistical mechanics has been the possibility of application to physical-chemical systems with many degrees of freedom corresponding to their many molecules, and the chief interest has been the practical one of elucidating the behavior of these complicated systems by a method that has elements of superiority over any other.

(3) *Comparison of the Methods of Statistical Mechanics and Thermodynamics.*—For the theoretical treatment of the behavior of complicated physical-chemical systems, the method of thermodynamics has been used in the past even more than that of statistical mechanics. A comparison of the nature of the two methods and some estimate of their relative advantages will be of interest.

If we first compare the two sciences as to the certainty of their foundation and the rigor of their development, the advantage most certainly lies with thermodynamics.

The whole of classical thermodynamics is based entirely upon two postulates, the first and second laws of energy, and must be regarded merely as the logical system of theorems which can be

[1] E. B. WILSON, *Annals of Math.*, 10, 129, 149 (1909).

drawn from these postulates by applying them to different types of physical-chemical systems. Moreover, the truth of the two fundamental laws, at least as far as the macroscopic behavior of physical-chemical systems is concerned, can hardly be questioned, deviations from the laws have never been found, and the whole past history of successful application furnishes a vindication of the starting-point. We must regard the theorems of thermodynamics as among the most certain possessions of science.

On the other hand, when we turn to statistical mechanics we find a much less certain foundation, and for parts of the science a less rigorous method of development.

The first underlying assumption, in the application of the science, is the hypothesis of the atomic and molecular structure of matter. This general hypothesis no longer has to withstand the attacks of the older school of physical chemists, influenced by Ostwald's point of view that the scientist should give attention only to observable phenomena. Nevertheless, just at the present moment, the physicists themselves, greatly influenced by the development of the general theory of relativity, which concerns itself only with observable space-time coincidences, are tempted to follow Heisenberg's lead in hoping that the difficult problems of the quantum theory can be solved by neglecting the atomic constitution of matter and concentrating attention solely on the observed relations as to the frequencies and intensities of spectral lines. In any case, even though we feel justified in accepting as one of our starting-points the general theory of atomic structure, we find in the course of our development of statistical mechanics many times a necessity for specific hypotheses as to the precise nature of atoms and molecules, which at the best can be regarded only as necessary simplifying assumptions.

Having started with the hypothesis of the atomic structure of matter, the method of statistical mechanics then consists in applying the laws of dynamics to determine the behavior of an ensemble of systems, each system itself composed of atoms and molecules. In the time of Gibbs and Boltzmann there would have been few to question this procedure. The laws of dynamics, as codified for example in the form of Hamilton's principle, are certainly a valid abstraction drawn from actual experiments on the behavior of moving bodies of macroscopic size, and the danger of applying these same laws to the motions of molecules

was then but dimly appreciated. To-day, however, the development of quantum theory has indicated that the most satisfactory treatment of atomic and molecular behavior may involve a complete revision of the laws of dynamics and perhaps even of our notions as to the continuity of space and time.

At the present time it seems best to try to solve this difficulty by first developing what may be called the classical statistical mechanics based on the older laws of dynamics. We can then regard this as a limiting case, valid when high frequencies of periodic motion are not involved, and later introduce, perhaps somewhat arbitrarily, those modifications which seem most suitable for the treatment of the great group of quantum phenomena.

One further lack of rigor in the method of statistical mechanics must be mentioned. Very early in the development, even of its classical applications to physical-chemical systems, we are forced to introduce the famous ergodic hypothesis, or principle of continuity of path. The introduction of this hypothesis is certainly justified by its results, and the reasons for its introduction in a suitably modified form can, as I shall hope to show you, be made plausible. Nevertheless, this hypothesis still presents a baffling problem for further study.

This concludes our statement of the sources of lack of rigor in the method of statistical mechanics. They are: First, the assumption of the atomic hypothesis itself, not so much the general assumption of the atomic structure of matter as specific assumptions as to atomic properties which must be made from time to time in the course of the development; second, the application of classical dynamics to describe the behavior of atomic systems, arbitrarily modified to take account of quantum phenomena rather than revivified by the newer dynamics which is yet to come, even though it is already heralded by birth pangs; and third, the introduction of the ergodic hypothesis which has to be made in order to make possible the important applications to physical-chemical systems that we desire to obtain.

It should be remarked that this lack of rigor is not resident in the science of statistical mechanics *per se*, but only arises when we come to actual applications to the problems of physics and chemistry. Nevertheless, we are interested in comparing the methods of thermodynamics and statistical mechanics as applied to actual physical-chemical systems, and for this purpose there

is no question that thermodynamics at the present time is superior as to rigor.

If we turn our attention now, however, to the results that can be achieved by the two methods, the balance is all in the favor of the newer science.

In the first place, as has been shown particularly by the work of Boltzmann and Gibbs, the two laws of thermodynamics may themselves be regarded as derivable from the principles of statistical mechanics and interpretable as the necessary result of atomistics. Hence all the possible conclusions of thermodynamics can in this way at least be indirectly obtained from statistical mechanics, although there are often advantages in their direct derivation, since the theorems then obtain a more intimate atomistic interpretation.

In the second place, the properties of matter enter the equations of thermodynamics merely as empirical parameters whose values have to be determined by actual measurements made upon macroscopic systems. In the treatments of statistical mechanics, however, the actual values of these quantities are often deducible from their atomistic interpretation. Thus, for example, in thermodynamic deductions, specific heats of gases and solids, heats of reaction and equilibrium constants enter the equations and are related one with another. Their absolute values remain, however, unknown. In statistical mechanical treatments, however, values of specific heats can be obtained from a consideration of the number of degrees of freedom of the system in question and the extent of their excitation; values of heats of reaction are gradually being related to the energy levels of atoms and molecules as determined from spectroscopy; and absolute values of equilibrium constants are obtained by considering the relative probability of different arrangements of the atoms to form molecules.[2]

In the third place, even in the field of equilibrium relations, for the treatment of which thermodynamics is specially fitted, laws arise which thermodynamics must use but cannot derive. Thus in particular the gas laws and the equations of state for matter in any form can for thermodynamics be only empirical facts, but

[2] The *third* law of thermodynamics essays this same task of determining absolute values of equilibrium constants. The correct formulation of the third law, however, involves statistical mechanical interpretation.

for statistical mechanics they are already either deduced or in any case deducible by methods we can now foresee.

In the fourth place, for a system which is not in equilibrium, thermodynamics can only tell us that those changes are permitted which involve an increase in entropy. It can give us no information as to the velocities with which the permitted changes will take place and hence in actuality usually gives us no prediction as to what will really happen in a system which is not in equilibrium. Thus such questions as rates of diffusion and evaporation, rates of thermal and electrical conduction, rate of momentum transfer, and rates of thermal and photochemical reaction, all lie beyond the power of thermodynamic reasoning. They are, however, amenable to statistical mechanical treatment.

Finally, when phenomena arise which are essentially atomistic in character, thermodynamics can of course have absolutely no help to give. The Brownian motion of particles, the fluctuations in the density of a fluid, the differences in the velocities of electrons from a hot filament, and the distribution of thermal radiation among its different frequencies, all furnish problems which statistical mechanics may treat, but which a non-atomistic thermodynamics must actually fail to recognize.

This long recital does not exhaust the achievements of statistical mechanics. It will give some idea, however, of the power of the method and the scope of its attack. The future of theoretical chemistry is dependent on its applications and there will be a mutual and advantageous interplay in the development of these two sciences.

We are now ready to proceed with the development of statistical mechanics. In the brief time available, all that I can hope to do is to sketch in outline the nature of the mode of attack, then state in an arbitrary fashion some of the results obtained, and consider some of the important applications which have been made.

(4) *Ensemble and Phase.*—As already stated, we shall not discuss the behavior of a single system, but rather the behavior of a collection or *ensemble* of systems, containing an enormous number of sample systems identical in nature with the one of interest. From the behavior of this collection of samples we shall then be able to draw conclusions as to the probable behavior of a single system.

The different systems in the ensemble will be of the same structure, that is, composed of the same numbers of atoms of each of the different kinds enclosed in similar containers, but will differ in the positions and velocities of their component elements. In the language introduced by Gibbs, they will be said to differ in *phase*.

If each system in the ensemble has m generalized coördinates $Q_1 \ldots Q_m$ and the corresponding m momenta $P_1 \ldots P_m$, then the instantaneous phase of a system could be specified by giving the momentary values of these m coördinates and momenta. Thus, for example, if we had a gas composed of N point particles flying around inside a container, we could take the m coördinates of the system as the $3N$ Cartesian coördinates x, y, and z for each particle, and the m momenta as the corresponding $3N$ components of linear momentum $m\dot{x}$, $m\dot{y}$ and $m\dot{z}$ for each particle. The reason for choosing the generalized coördinates and momenta rather than coördinates and velocities will later become apparent.

(5) *Phase Spaces.*—To follow the behavior of such a system, that is its change in phase with time, it is very convenient to think of its phase as given by the position of a representative point (phase point) in a 2-m dimensional space (phase space) corresponding to the 2-m coördinates and momenta whose values are to be specified. As time proceeds the phase point for a given system will describe a trajectory in this 2-m dimensional phase space, and the phase points for all the systems of an ensemble can be regarded as describing stream lines in the space. This device has the advantage of providing a ready-made geometrical language for discussing the behavior of the ensemble.

If our system is composed of molecules, it is also often convenient to represent the values of the coördinates and momenta for a single molecule, in a phase space of a smaller number of dimensions than that necessary for the whole system. Thus the phase of a single molecule having the 2-n coördinates and momenta $q_1 \ldots q_n$, $p_1 \ldots p_n$, could be represented by the position of a point in a space of 2-n dimensions.

In order to avoid the possibility of confusing these two different phase spaces, it will sometimes be convenient to employ the nomenclature of Ehrenfest and call the phase space used for

representing the condition of the whole system or "gas" a γ-space, and the phase space for a single molecule a μ-space.

For example, if our system is built up of N monatomic molecules, the phase space or μ-space for each molecule would have six dimensions corresponding to the three coördinates and three momenta which specify the state of such a molecule. Thus, if I have a set of axes as shown on the chart, I could plot the x coördinate for a given molecule as an abscissa and the corresponding momentum, $m\dot{x}$, as an ordinate. I could then take an axis perpendicular to the chart for plotting values of the y coördinate and a fourth dimensional axis perpendicular to the first three for plotting values of $m\dot{y}$ and then two more fifth and sixth dimensional axes for z and $m\dot{z}$. The fact that I cannot construct an actual six-dimensional space for plotting my point does not prevent the use of the convenient geometrical language which this conceptual method presents.

Having finished with the first molecule, I can now go on and put in six more axes for each of the remaining $N-1$ molecules and thus obtain a $6N$ dimensional phase space or γ-space for the whole gas. The position of a point in this final γ-space will then represent the instantaneous positions and momenta for all the molecules of the gas, and as the molecules fly around and collide with each other and the walls, the representative point will move around in this γ-phase space in a way determined by the laws of mechanics.

(6) *Distribution of the Ensemble in Phase.*—If we return now to our whole ensemble of systems, it is evident that each system in the ensemble will give us a point in the γ-space. We may initially distribute these points in any way we desire, and then follow their motion as they describe stream lines in this space. We shall define the density of distribution ρ at any position in the phase space as the number of points per unit $2n$ dimensional volume at the position in question.

Different methods of initially distributing the points in the phase space can be used for different purposes. The three distributions that have been most employed are the *canonical ensemble* introduced by Gibbs and used by him and others,

$$\rho = Ne^{\frac{\psi - E}{\theta}}, \qquad (1)$$

where N is the total number of systems in the ensemble, E is the energy of a single system, and ψ and θ are constants having the dimensions of energy; the microcanonical ensemble used by Gibbs, Boltzmann, Jeans and others,

$$\rho = \text{const.} \quad \text{(when the energy lies between } E \text{ and } E + dE\text{)}$$
$$\rho = 0 \qquad \text{(for other values of the energy)} \tag{2}$$

and the *surface ensemble* used by Ehrenfest, in which the phase points are distributed on a surface in the γ-space of constant energy with the surface density

$$\sigma = \frac{\text{const.}}{\sqrt{\left(\frac{\partial E}{\partial Q_1}\right)^2 + \cdots\cdots + \left(\frac{\partial E}{\partial P_m}\right)^2}}. \tag{3}$$

The nature of these three distributions is indicated by the figure on the chart. The curve AB is to be thought of as representing a surface in the γ-space of constant energy E, and the shading in the neighborhood of this curve represents the density of distribution.

All three of these distributions can be used for drawing conclusions as to the probable behavior of a single system.

The surface ensemble would at first sight seem to be the most suitable for this purpose, since all the systems of the ensemble could be given the same energy as that of the system of interest. From the point of view of mathematical simplicity, however, the surface distribution is not as easy to handle as the others, and we shall not employ it in the present lectures.

From many points of view, the canonical ensemble of Gibbs is mathematically the simplest and theoretically the most illuminating. Its use, for predicting the behavior of a single system, is dependent on the fact that most of the systems in the ensemble will be found to have an energy sensibly equal to the average energy for all the systems in the ensemble, the fluctuations in energy being of the order that might be expected for a system placed in a thermostat, so that heat could flow in and out of it at will. Hence a system picked at random from the ensemble may be regarded as a fair sample of a single system left to itself. The canonical ensemble has also been of great value in showing the relation between statistical mechanics and thermodynamics, a field, however, which we cannot enter in these lectures.

The microcanonical ensemble is the one which has been most employed, and is the most satisfactory for our purposes. By taking the energy range dE, within which the phase points are distributed in the γ-space, as small as we desire, we can give all the systems sensibly the same energy, and shall find that we can then regard a system picked at random from this ensemble as a fair sample of a single system left to itself with an energy content within this small range. Most of the practical discoveries in the field of statistical mechanics have been obtained from a consideration of the behavior of microcanonical ensembles.

(7) *Change in Density of Distribution with the Time. Liouville's Theorem.*—So far we have merely said how we may *initially* place the representative points, for the systems of an ensemble, to obtain the three distributions known as canonical, microcanonical and surface, and haven't yet said anything about the further behavior of these points. Evidently we must at least know what is going to happen to the density of distribution ρ in order to use these ensembles for drawing conclusions. The investigation of this important problem is made possible by the fact that the motion of the points in the phase space is of course directly related to the motion of the individual systems of the ensemble and these motions in turn are governed by the laws of mechanics.

As a matter of fact, the problem of the change in the density of distribution can be treated for any arbitrary original distribution of the points, the result being known as Liouville's theorem. For our purposes we shall only need to consider one specially simple case of Liouville's theorem, namely, what will happen to the ensemble if we originally distribute the points with uniform density throughout the phase space.

To investigate this let us consider some particular cubical element in our phase space $dQ_1 dQ_2 \ldots dQ d_m P_1 dP_2 \ldots dP_m$, and turn our attention to the pair of opposite faces perpendicular to the Q_1 axis. The area of each of these faces, which are located at the distance dQ_1 apart, is evidently $dQ_2 \ldots dP_m$. Hence for the number of points entering the first of these faces located at Q_1, we can evidently write

$$\rho \frac{dQ_1}{dt} (dQ_2 \cdots dP_m) .$$

And for the number leaving the opposite face located at $Q_1 + dQ_1$, we can write

$$\rho\left(\frac{dQ_1}{dt} + \frac{\partial}{\partial Q_1}\frac{dQ_1}{dt}dQ_1\right)(dQ_2 \cdots dP_m).$$

Subtracting the second expression from the first, we obtain for the net gain per second in the number of points inside the cubical element

$$-\rho\left(\frac{\partial}{\partial Q_1}\frac{dQ_1}{dt}\right)(dQ_1 dQ_2 \cdots dP_m).$$

We can now proceed in a similar fashion to the other pairs of parallel faces and, adding, obtain for the total change in number of points per second,

$$\frac{dN}{dt} = -\rho\left(\frac{\partial}{\partial Q_1}\frac{dQ_1}{dt} + \cdots + \frac{\partial}{\partial Q_m}\frac{dQ_m}{dt} + \frac{\partial}{\partial P_1}\frac{dP_1}{dt} + \cdots + \frac{\partial}{\partial P_m}\frac{dP_m}{dt}\right)(dQ_1 \cdots dP_n),$$

or dividing by the volume of the element, $dQ_1 \ldots dP_m$, can write for the rate of change of the density inside our element

$$\frac{d\rho}{dt} = -\rho\left(\frac{\partial}{\partial Q_1}\frac{dQ_1}{dt} + \cdots + \frac{\partial}{\partial Q_m}\frac{dQ_m}{dt} + \frac{\partial}{\partial P_1}\frac{dP_1}{dt} + \cdots + \frac{\partial}{\partial P_m}\frac{dP_m}{dt}\right). \tag{4}$$

The values of dQ_1/dt, dP_1/dt, etc. . . ., however, are known from the equations of motion, which for any dynamical system can be written in the Hamiltonian form

$$\frac{dQ_i}{dt} = \frac{\partial H}{\partial P_i} \qquad \frac{dP_i}{dt} = -\frac{\partial H}{\partial Q_i}, \tag{5}$$

where H is the energy of the system expressed as a function of the coördinates and momenta. Hence we have

$$\frac{\partial}{\partial Q_1}\frac{dQ_1}{dt} = \frac{\partial}{\partial Q_1}\frac{\partial H}{\partial P_1} \tag{6}$$

and $$\frac{\partial}{\partial P_1}\frac{dP_1}{dt} = -\frac{\partial}{\partial P_1}\frac{\partial H}{\partial Q_1}.$$

And, since the order of differentiation is immaterial, we see that substituting pair by pair into equation (4), we shall finally obtain the fortunate result

$$\frac{d\rho}{dt} = 0. \tag{7}$$

In other words, if we start with our representative points uniformly distributed in the phase space, they will permanently maintain this uniform distribution. Furthermore, since a given system cannot change its energy in the course of its motion, it is evident that the density of distribution will remain unchanged with time if the phase points are distributed as any function of the energy, but uniformly in each region between the limits E and $E + dE$. So that we may write

$$\frac{d\rho}{dt} = 0$$

whenever the distribution is merely a function of the energy of the systems.

Such ensembles, in which the density of distribution does not change with the time, are said to be in *statistical equilibrium*. It will be noted that the canonical and microcanonical distributions mentioned above would evidently give ensembles which are in statistical equilibrium, and it can also be shown that the surface distribution would also be in statistical equilibrium.

The possibility of obtaining this significant result is dependent on our choice of generalized coördinates and *momenta* as the 2-m axes for our phase space. If we had plotted our representative points in a phase space in which the axes were the coördinates and *velocities*, we should not in general have been able to achieve so simple a result, since we could not then have obtained the simplification arising from the introduction of equations (5), which are dependent on the use of the equations of motion in the Hamiltonian form involving the generalized momenta. This is the reason why the equations of motion in the canonical Hamiltonian form are so important for statistical mechanics and why in statistical mechanical work momenta rather than velocities practically always appear in the expressions we obtain. It is

to Boltzmann that we owe the clear recognition of the importance of using momenta in statistical mechanical considerations.

(8) *Application to Molecular Systems.*—The foregoing simple result provides nearly all that is necessary for the application of statistical mechanics, and we are now ready to discuss the behavior of actual systems of molecules.

Let us consider a system of molecules enclosed in a suitable container and having the energy content E. In general this energy content, and the components of linear and angular momenta of the whole system, which we shall take as zero, will be the only dynamical quantities of which we have any knowledge, since the motions of the individual particles are too complex for us to follow.[3] Hence, since we do not know the precise molecular configurations and velocities of our system, we must consider all possible phases that such a system with the known energy content E might assume, and to do this we can use a microcanonical ensemble of systems similar to the one of interest with their representative points distributed uniformly throughout a shell which lies between the surfaces determined in the 2-m dimensional space by E and $E + dE$.

(9) *Introduction of the Ergodic Hypothesis.*—So far we have proceeded without the introduction of any hypotheses, except that the system obeys the laws of dynamics in the canonical form. To go further, however, we must now introduce the assumption that such a microcanonical ensemble of systems having energies between E and $E + dE$ gives a fair representation of the different phases which will be assumed in the course of time by a single system having an energy content between E and $E + dE$. To state this more specifically we shall have to assume that the results obtained by selecting a collection of systems at random from such an ensemble are practically the same as would be obtained by considering a given system at random times.

A certain empirical justification for this assumption is given by the fact that so many later developments based on its use are found to meet the test of experiment.

[3] The fact that they are beyond the powers of our observational methods is a secondary matter. The methods would be just as necessary in the case of a system of equal complexity even if composed of particles of size large enough to observe easily.

The theoretical justification for the assumption is more difficult and less certain, though nevertheless plausible.

In the first place, it should be noted that the maintenance of uniform density in a microcanonical ensemble, guaranteed by equation (7), means that the representative points for the systems have no tendency to crowd into any particular region of the phase space. If such a crowding did take place, the representative point for any given system would at any arbitrary time be more likely to lie in such a region of compression than elsewhere in the phase space. In the absence of such crowding, however, we can definitely state that a *given system taken at any random time has an equal chance of being in any one of the different microscopic states through which it actually passes in the course of its history.*

This definitely valid conclusion is, of course, however, not identical with the statement that the system has an equal chance of being in any one of all the microscopic states which lie in the phase space between the surfaces determined by E and $E + dE$, since a given system may not in the course of its complete history be able to reach all the regions between E and $E + dE$.

To meet this the *ergodic hypothesis,* as it was called by Boltzmann, or the *principle of continuity of path,* as it was called by Maxwell, makes the definite assumption that a system of molecules actually does pass through all possible microscopic states consonant with its energy content before completing its cycle of motions. This hypothesis, if true, would of course make the selection of random samples from a microcanonical ensemble absolutely identical with the consideration of a given system at random times and hence would justify the further procedure we wish to undertake.

The ergodic hypothesis in its simple form, however, is not even plausible. The reëntrant orbits of astronomy have made us quite familiar with the possibility of an infinite number of closed paths for a given dynamical system all of them having the same energy content. Indeed, no single example of a dynamical system of more than one degree of freedom has ever been discovered in which the motion carries the system through all possible phases consonant with its energy content.

It seems evident that we must reject the ergodic hypothesis in its simple form as not having sufficient plausibility and investigate

other similar assumptions which would lead to equivalent results. We may consider three further simple possibilities.

(*a*) It might be assumed that for a system of molecules with a given energy content there are a number of closed paths possible, but that one of them is infinitely longer than all the others put together, so that we could neglect the possibility of the system being on any path but the longest, and the microscopic states lying along this path would include practically all the microscopic states in the region between E and $E + dE$. Such a possibility was apparently first suggested by Jeans, but we must agree with him in rejecting it as being no more plausible than the assumption of a single closed path itself.

(*b*) A second possibility would be to assume that for a given energy content a system of molecules can move on any one of a number of closed paths, but cannot of itself get from one of these closed paths to another. It might, however, be fortuitously removed from one path to another by external agencies in such a way as to have an equal probability of being in any microscopic state belonging to any system in the corresponding microcanonical ensemble. This point of view has also been suggested by Jeans, who has further indicated the plausibility of regarding one of the molecules themselves as a fortuitous external disturbing agency which acts on the system, which is now regarded as composed of all the other molecules present. This assumption would of course lead to the desired results.

(*c*) A third possibility, which appears to me to be the most satisfactory for the purposes at hand, is to grant that there may indeed be more than one closed path for the motion of a system of molecules, with a given energy content—perhaps indeed a great many such paths. Lying along each closed path will be a succession of microscopic states, through which the system must pass before it rearrives at the starting-point; this, however, it will inevitably do, since we shall take the regions $dQ_1 \ldots dP_m$ which specify the different microscopic states as small but nevertheless finite, so that there will not be an infinite number of possible states.

Let us now consider the motion of a given system when left to itself. Its representative point will have to lie on one of the possible paths which correspond to its energy content. We cannot say on which path, but, as we saw above, we can say that at

any random time it has an equal chance of being in any one of the microscopic states that lie along this particular path.

So far we have introduced no assumption. Let us now consider, however, the probable nature of the different closed paths. It is evident that for an actual system containing many molecules, most of these closed paths would have to be very long. Consider, for example, a gas composed of many molecules moving back and forth between the walls of its container. Even if the molecules collided only with these walls and not among themselves, it is evident that we should have to wait an exceedingly long time before we should again find every individual molecule back at its starting-point, and when we allow for collisions among the molecules themselves, the time is enormously longer yet. Hence at least the vast majority of the paths will contain an enormous number of microscopic states taken out from those that lie in the total shell between E and $E + dE$.

It hence seems reasonable, since so many states have to be taken, to assume, by and large, that the microscopic states lying along the particular closed path on which the system of interest happens to lie are themselves a fair sample of all the different kinds of states present in the whole region of phase space between the limits E and $E + dE$. If this be admitted, any large collection of samples chosen at random from the whole microcanonical ensemble between E and $E + dE$ will have practically the same properties as a collection obtained by observing the given system at random times, and the use of the microcanonical ensemble as giving a fair representation of the succession of states arrived at in time by a single system is justified.

Thus, for example, in the case of a gas, it is possible to show that the vast majority of all the states in the corresponding microcanonical ensemble have distributions of molecular velocities that do not differ appreciably from Maxwell's law. Hence, we then feel justified in believing that this is also probably true for the vast majority of the states lying along the particular path on which a given sample of the gas is to be found.

We shall henceforth proceed on the assumption that a microcanonical ensemble may be taken as giving a fair representation of the successive states of an actual molecular system.

I hope that this description of the starting-point for statistical mechanical investigations which I have given you has not seemed

too involved and technical. The use of a space of more than three dimensions, and indeed a space of $6N$ dimensions, where N is of the order of a trillion, for plotting the position of a point, seems at first sight a very terrifying notion. It is, however, merely a device for providing a familiar geometrical language as a shorthand for talking about analytical quantities, and as early emphasized by Gibbs, the results can, as a matter of fact, all be obtained without ever employing any language foreign to analysis itself.

I feel sure that in any case you have grasped the main features of the method. A single system containing many atoms and molecules is so complicated that we cannot hope to follow or describe its precise behavior. Hence we turn to the consideration of a whole ensemble of systems similar in structure to the one of interest, but with their molecules arranged in all possible different ways consonant with the energy of the system. By studying the *statistical behavior* of such an ensemble we can then make predictions as to the *probable behavior* of a single system. You can easily see that this introduces a powerful method into a very difficult field. The future development of most of theoretical chemistry and much of theoretical physics will, I feel sure, be intimately dependent on the use of statistical mechanics.

In the next lecture I shall try to describe some of the results that we can obtain by applying statistical mechanics to systems of molecules which are in equilibrium.

SOME EFFECTS OF DILUTION AND STIRRING OF A PHOTOGRAPHIC DEVELOPER.*

BY

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GENERAL DISCUSSION.

IT HAS often been assumed that if a given developer were diluted, the times of development required at different concentrations would bear a simple relation to the relative concentrations of the solutions. For example: A developer of a certain strength which would require three minutes development, on dilution to one quarter that strength would require four times as long development, or twelve minutes. This assumption may be stated more clearly as follows:

$$T_{dev} = k\,Dil,$$

where T_{dev} is the time of development, k is a constant, and Dil is the relative dilution. This can also be written

$$CT_{dev} = k,$$

where C is the relative concentration of the developer.

In applying this rule to the experiments below, the relative concentration or dilution is used, *i.e.*, the developer at some particular strength is arbitrarily assigned unit concentration or dilution. The experiments described here show that wide deviations occur from the assumption stated above, depending on the concentration range used, the nature of the developing solution, and on other factors.

Our purpose was to investigate these deviations and if possible to determine their cause. The present work represents only a partial investigation of the subject carried out in one of the plant laboratories. The material is published largely to record results obtained and to suggest additional experimental work where possible. Except for minor fragments, practically no available work was found in the literature covering effects of dilution of developers.

* Communicated by Dr. C. E. K. Mees, Director of Laboratory, and published as Communication No. 288 from the Research Laboratory of the Eastman Kodak Company.

On developing in solutions of different strengths strips which had been exposed behind a sensitometric tablet, reading the densities, and then plotting the density for a given exposure against the logarithm of the relative dilution, a curve of the general type shown in Fig. 1 was obtained.

The strips for each dilution were developed the length of time required by the rule. If the rule held as at first supposed, the density would remain constant irrespective of the dilution, that is, the curve would be a horizontal straight line.

Again, it was found that strengthening a certain pyro tank formula did not increase the density or contrast as expected. As the solution was strengthened the density increased slightly, and then decreased when the solution was made stronger. The falling off of density from either side of a maximum (Fig. 1) led to certain difficulties in explaining the phenomena. We first attempted to explain the first part of the curve, where the density increases as the dilution is increased, and thought the falling off of the second part of the curve, where the density falls off with increasing dilution, due to entirely different causes.

After numerous experiments it was decided to consider all factors which might produce any variation from the dilution rule first stated.

These factors are:

(1) Penetration effects due to surface development (tanning) and to oxidation products in the emulsion layer (local exhaustion).
(2) Penetration effects due to swelling.
(3) The effect of excess of reducing agent.
(4) Aerial oxidation of the more dilute solutions.
(5) Possible variation of reducing energy with concentration.
(6) Hydrolysis.
(7) Effect of more vigorous stirring (probably connected with 1).

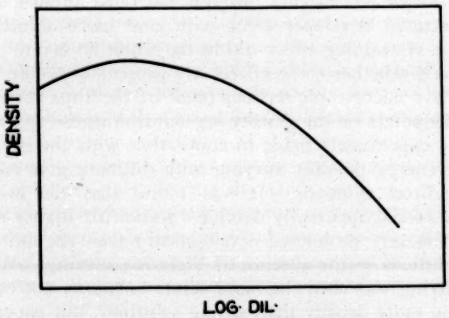
Curves of the type of Fig. 1 were obtained by occasional stirring as in common tank methods. With more vigorous stirring the effect of some of the factors mentioned was changed or partially eliminated. We will therefore consider first the influence of these factors where development is carried on in the usual manner, with no mechanical stirring devices, and later

the modifications brought about by such mechanical stirring will be discussed.

EXPERIMENTAL DETAILS.

The general method employed was to make exposures under constant conditions behind a sensitometric tablet of practically neutral color and known transmission. The light source was a gas-filled tungsten lamp. The films were developed for accurate times, hanging vertically in tall beakers filled with developer. The temperature was maintained practically constant, 64° to 66° F., by regulation of the room temperature. The films were

FIG. 1.



General effect of dilution (for a given exposure).

moved occasionally to provide stirring and some were developed with the light and some with the heavy densities at the top to be sure that no convection effects occurred. After reading the strips and plotting the usual H and D curves for the two duplicate films, the density at a fixed exposure was read from the curve and then plotted against the logarithm of the relative dilution.

The negative material used throughout was Eastman Commercial Film. This was chosen because it accentuated the differences in density and contrast and was free from fog. Other materials were also tried to prove that the negative material had no effect on the shape of the density-log dilution curve except through differences in contrast. The other materials used were Kodak Film Pack, Kodak N. C. Film, Eastman 40, and Hammer Special Plates. These showed, with an elon developer diluted in

the usual manner, the same general density-log dilution curve, differing only in degrees of contrast.

DISCUSSION OF RESULTS.

(1) Penetration effects due to surface development (tanning) and to oxidation products in the emulsion layer.

The opinion has been held that a concentrated developer acts mostly at the surface because rapid tanning action would occur at this point, retarding or partially preventing diffusion of the developer into the gelatin. This would consequently cut down the total density which might be developed.

Further, the oxidation products would more likely be retained by, and diffuse less rapidly through, the outer tanned layer with a concentrated developer than with one more dilute, thereby exerting a restraining effect within the emulsion layer. To prove conclusively whether these effects are present, it would be necessary to have microscopic sections made of the films corresponding to various points on the density-log dilution curve.

Later experiments made in connection with the effect of the reducing energy possibly varying with dilution, give some interesting indirect evidence. It was found that the more dilute developers could apparently develop a somewhat higher maximum density (on very prolonged development) than the more concentrated solutions in the absence of vigorous stirring. When very rapid stirring was used the more dilute solutions not only failed to develop more density than strong solutions, but appeared even weaker, probably because of aerial oxidation, as discussed below.

It therefore appears that without strong stirring effects of surface development and local exhaustion may occur in concentrated developers. As these effects would tend to prevent complete development of the latent image, they would make it appear that the dilute solutions could develop a higher maximum density, as shown in Table I, p. 524.

If rapid stirring is employed, the emulsion would be subjected to vigorous washing which would tend to diminish the effect of surface tanning and local oxidation. This is what occurred experimentally. The fact that the more dilute solutions gave a higher maximum density, without stirring, than the concentrated solutions, might have been caused in part by the effects of varying degrees of swelling or of hydrolysis. As the rapid stirring seemed to lessen the difference between the concentrated and

dilute solutions as first found, it would seem that swelling and hydrolysis had had only a partial effect and that surface development and local exhaustion had been largely responsible for the difference. An idea of the extent to which local exhaustion affected the result will be obtained from the section on stirring.

(2) Penetration effects due to swelling.

The swelling of the gelatin film would, of course, be greatly variable according to the nature and concentration of the solution. It is well known that the swelling of gelatin varies with the hydrogen-ion concentration, being a minimum at a certain hydrogen-ion concentration which is usually near the neutral point, according to the particular sample of gelatin. Neutral salts and other substances may have specific effects on swelling.

If the developing solution concerned contains a certain amount of sodium carbonate or sodium hydroxide, as is usually the case, on diluting this developer, we pass over a wide range of hydrogen-ion concentrations, and this range may be within the range where the swelling of gelatin varies rapidly. Further, we have present widely varying concentrations of certain neutral salts which may add to or complicate the effect on the whole curve.

To determine whether swelling played an important part, films were first developed in developers which were widely different and the films were specially treated to soften or harden the gelatin.

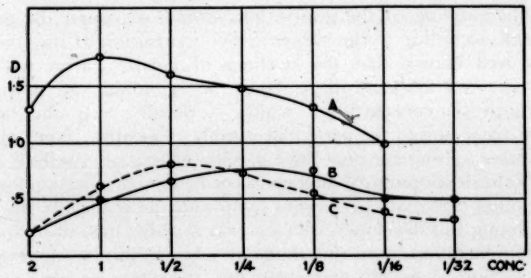
First, three hydroquinone developers were used, made up as follows:

Formula.	Hydroquinone.	Sodium Sulphite.	Sodium Carbonate.
No. 1	5.5 gm. per litre } M/20	50 gm.	50 gm.
No. 2	5.5 gm. per litre }	50 gm.	Sodium Hydroxide 8 gm.
No. 3	15 gm. per litre	50 gm.	Formaldehyde (40%) 20 c.c.

These three developers, of course, produced in the gelatin widely different degrees of swelling. While indirect evidence, it is likely that some differences would be found between strips which had been hardened and those which had been softened. No differences in the shape of the density-log dilution curve from the normal were noted. Fig. 2 shows the results for each of the three formulas, which differ only in the convexity of the curves. Curve *A* is for formula 2, *B* for formula 1 and *C* for formula 3.

Next films were developed in an ordinary developer[1] at various dilutions, some of the films having been previously soaked in sodium hydroxide solution. Though a concentration (0.25 M) of caustic soda which would cause considerable swelling was

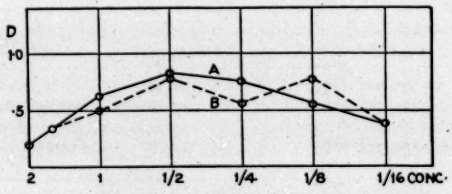
FIG. 2.



Dilution curves for three widely different hydroquinone developers.

used and the time of soaking was varied, there was very little difference between the curves obtained by that and the ordinary methods. (See Fig. 3, curve *A*, soaked in sodium hydroxide, curve *B*, untreated.) Naturally the gelatin would not remain at

FIG. 3.



Effect of pre-swelling on dilution curve.

the same degree of swelling when transferred from the caustic soda solution to another solution, but would nevertheless be much different from gelatin not given the swelling treatment.

The next experiment tried was to vary the dilution of all con-

[1] Hydroquinone Formula No. 1 above. One set of films was soaked fifteen minutes in 0.25 M sodium hydroxide, washed five minutes and then developed. The other set was developed in Formula No. 1 without treatment.

stituents of the developer in the ordinary way, but keep the concentration of the alkali always the same. A number of experiments made in this way still gave the same type of density-log dilution curve.

Fig. 4 was obtained with formula 4 below, curve *A* being obtained by the normal developer at regular dilutions, and curve *B*

FIG. 4.

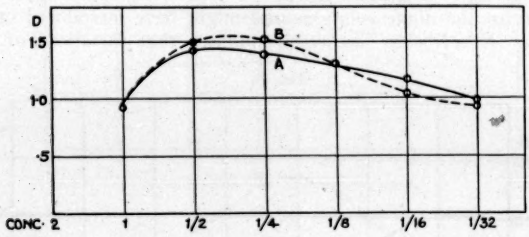
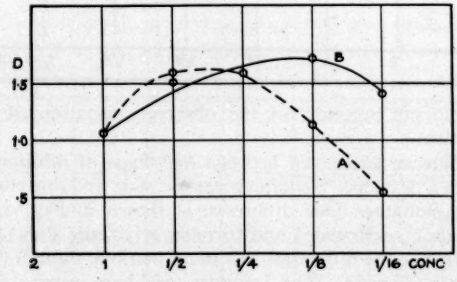


FIG. 5.



by diluting the developing agent and sulphite, but keeping the carbonate concentration constant at 50 gm. per litre.

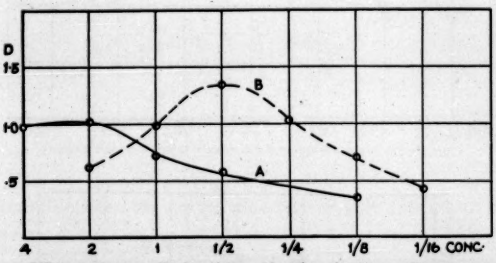
Formula.	Paramidophenol M Hydrochloride $/_{20}$.	Sulphite.	Carbonate.
No. 4	7 gm. per litre	50 gm.	50 gm.

Fig. 5 shows a similar result for formula 1, p. 513. Curve *A* was obtained with regular dilution of the developer and for curve

B the carbonate concentration was kept constant at 50 gm. per litre as for Fig. 4, curve *B*.

A similar experiment was made with a caustic hydroquinone developer (formula 2) keeping the alkali constant. This did not change the shape of the dilution curve materially. Naturally the conditions here were slightly changed, the solution not having been in exactly the same state chemically as when diluted in the ordinary way. The ratio of alkali to developing agent was much higher for the dilute solutions and might have introduced other effects. Nevertheless, the results indicate that variations of the

FIG. 6.



Differences between dilution with caustic soda and sodium carbonate.

swelling do not account for the observed variation of density with dilution.

A difference was noted between the shape of dilution curves made with a developer containing caustic soda and one containing sodium carbonate. This difference is shown in Fig. 2, curves for formula 1 (carbonate) and formula 2 (caustic soda), p. 513. In another case the difference was more marked, though the same in character (Fig. 6). The formulas used here were:

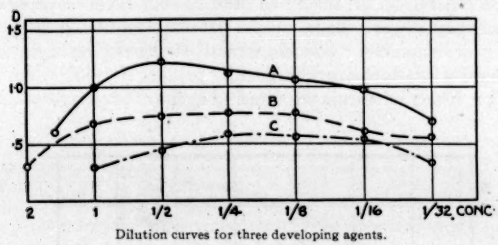
Formula.	Hydroquinone.	Alkali.	Sodium Sulphite.
No. 5	5.5 gm. per litre	2 gm. NaOH	25.2 gm.
No. 6	5.5 gm. per litre	50 gm. Na_2CO_3	25.2 gm.

Curve *A* is for formula 5 and *B* for formula 6.

As so many factors influence the shape of the dilution curve, the above difference cannot be explained for the present.

Different developing agents do not give exactly the same curves, some having very little rise in density at the beginning and others differing in the concentration at which the density is a maximum. Fig. 7 gives dilution curves for elon (curve *A*, for-

FIG. 7.

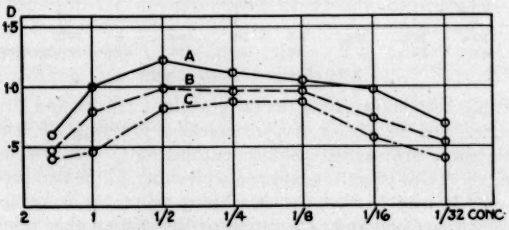


Dilution curves for three developing agents.

mula 7 below), pyro (curve *B*, formula 8), and glycin (curve *C*, formula 9).

Formula.				
No. 7	Elon 8.5 (M/20)	Sodium carbonate 50	Sodium sulphite 50
No. 8	Pyro 6.3 (M/20)	Sodium carbonate 50	Sodium sulphite 50
No. 9	Glycin 8.4 (M/20)	Sodium carbonate 50	Sodium sulphite 50

FIG. 8.



Curves for three different times of development.

The difference in density between the maximum and minimum is dependent on the time of development employed, as shown by Fig. 8, which is for formula 7 (above) at three different times of development at unit concentrations.

Or, referring to the rule (p. 509)

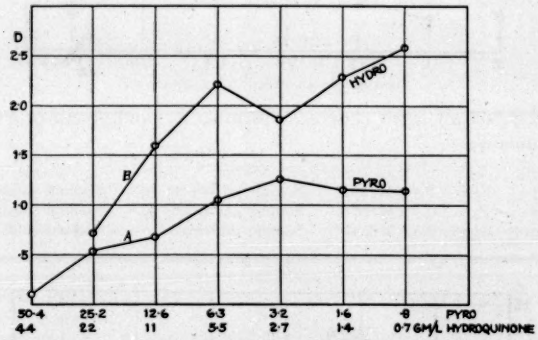
$$CT_{den} = k,$$

the value of T_{dev} at $C = 1$, is taken in this experiment as equal to 1, 1½, and 2 for the three curves *A*, *B*, and *C*, respectively. The location of the maximum is unchanged.

The effect of the developing agent on the swelling is not known, as already stated. A great deal of very useful information bearing on the theory of development could be procured if measurements were made of the swelling of the gelatin layer during development. Specific effects of developing agents may be found when such work is done.

(3) Effect of excess of reducing agent.

FIG. 9.



Effect of excess of developing agent.

It has been known since the early work of Hurter and Driffield appeared that an excess of pyro causes a lowering of density.[2] While there are several possible explanations, it is not known definitely if this effect is connected with either of the two previous causes. It may be that the developing agent has some specific effects on swelling and penetration or has still another rôle.

The actual photographic effect of an excess of reducing agent was determined. Fig. 9, curve *A*, shows results in pyro, curve *B*, with hydroquinone. The solution consisted of, per litre, sodium carbonate 50 grams, sodium sulphite 50 grams, and pyro is added in varying amounts as indicated by the upper row of figures for the abscissæ. The figure shows a marked reduction in density

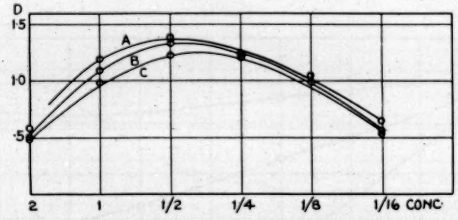
[2] HURTER and DRIFFIELD, *Phot. Jour.*, 1898, 186.

when too much pyro is present. It is evident that this phenomenon may be partially responsible for a decrease in density at the higher concentrations of an ordinary developer. Fig. 9, curve *B*, is similarly for hydroquinone, the solution consisting of sodium hydroxide 8 grams, sodium sulphite 50 grams per litre, the hydroquinone concentration being indicated by the lower line of values under the figure.

(4) Aerial oxidation of the more dilute solutions.

If a developer is diluted with ordinary tap water or distilled water, the water itself will contain so much dissolved oxygen that

FIG. 10.



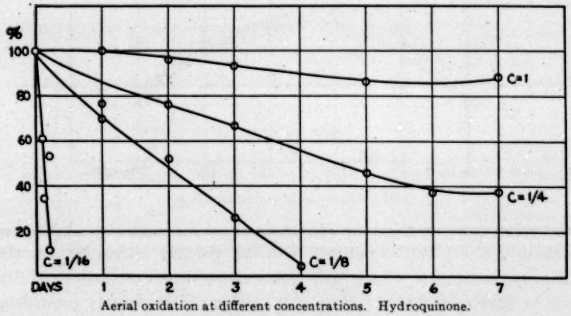
Effect of saturating developer with air.

the relative proportion of the oxygen in the water to the active constituent of the developer will be greatly increased as the dilution increases. This will cause more rapid oxidation of the dilute developer and a consequent falling off in density providing the oxidation has taken place rapidly enough. Experiments described below show that this more rapid oxidation is easily found at high dilutions, but that when all ordinary precautions are taken it is too slow to affect the density given by a fresh developer, and it is by no means the principal factor in determining the shape of the second portion of the curve. It was first suggested that such oxidation entirely explained the decrease in density. A number of experiments showed this not to be the case. Water which was relatively freed from oxygen by boiling at low pressure, and water saturated with air by bubbling air through it for eighteen hours, were compared as to effect on dilution curves. Formula 1 (hydroquinone) was used and the result is seen in Fig. 10. Curve *A* is for water free from air, curve *B* for water saturated with air and allowed to stand four

hours, curve *C* also water saturated with air. Practically no difference is observed for the various conditions. In the first two experiments the developers were used directly after mixing. A third experiment was carried out with water saturated with air as above, the developer then made up, and the solution allowed to stand four hours. If, however, the solutions had been allowed to stand for a much longer time, those saturated with air would deteriorate more rapidly than that relatively free from air. In this case the difference caused by four hours' standing was small.

More careful experiments were made to determine the length of time required to show the oxidation effect at different concen-

FIG. 11.



Aerial oxidation at different concentrations. Hydroquinone.

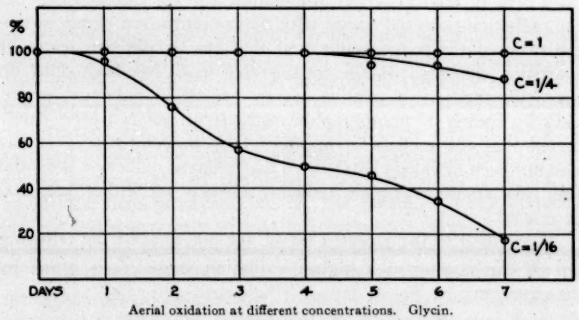
trations. Fig. 11 shows the relative densities developed by different concentrations of a standard hydroquinone developer (formula 1) when the solutions are allowed to stand for varying lengths of time. The ordinates are expressed as a percentage of the density developed when the developer is absolutely fresh. The abscissæ are times in days.

It is seen that the more concentrated developer gives practically the same density throughout the entire period it was followed, but that as the concentration becomes less the density falls off more and more rapidly. When the developers were used immediately after diluting, however, the results were found reliable, and all developers were so used throughout the experimental work. It was concluded that aerial oxidation was only in small part responsible for the effect shown by the dilution curve.

The last experiment (Fig. 11) proved of great interest when tried with other developing agents, although the matter was but slightly touched. Results obtained show that developing agents vary much more in their resistance to oxidation when highly diluted than is commonly supposed from the usual comparisons made at relatively high concentrations.

It is suggested that practical investigations of the keeping powers of developers be made in the manner described for the above experiment. This method has great advantages for comparison of different developers, as shown by results for hydroquinone and glycin, as it gives positive results within a reasonably

FIG. 12.



Aerial oxidation at different concentrations. Glycin.

short time. Glycin, for example, shows its difference in stability from hydroquinone much more quickly and clearly at a concentration of one-sixteenth than it would at normal concentrations.

The curves for glycin are shown in Fig. 12 (compare with Fig. 11).

(5) Effect of reduction potential.

In previous work by one of the writers,[3] the term "reduction potential" was used to define relative photographic reducing energy. This quantity was determined for a number of reducing agents by making use of the effect of potassium bromide in lowering the density under certain conditions. The term "reduction-potential," as previously used, is not necessarily identical with electrochemical reduction potential and for that reason it would

[3] A. H. NIETZ, "The Theory of Development," E. K. Monograph No. 2.

probably be preferable to adopt, for the time being, the term "relative reducing energy" when applied photographically. It was suggested to the writers that the actual reducing energy of the developer might be lowered when the developer was highly diluted. This was considered apart from the previously mentioned effects. In other words, it assumes that the reducing energy of the developer decreases with concentration. The assumption was made that the developer of lower reducing energy would develop less of the latent image finally, and would possess a lower velocity initially, giving less density within the required time. Were this true, there would be no relation between "reduction potential" in its strict sense and "reducing energy."

There is no theoretical foundation for the assumption that the reduction potential varies with the concentration except where the ratio of the concentrations of the ions of the two states of oxidation changes. While considerable work has been done on the determination of relative energy (so-called reduction potential) by means of photographic methods, it has not been determined that the method is unaffected by concentration. It has also not been definitely established that relative reduction potential and relative photographic reducing energy are either identical or related.

According to the accepted views, the potential of the reducing ion $\overline{R}$ in passing to a higher oxidation stage $\overline{R}$, is given by the equation

$$E = RT \log \frac{\overline{R}}{\overline{R}},$$

where $\overline{R}$ and $\overline{R}$ are concentrations of the two species of ions. This relation shows that the reduction potential depends on the ratio of the concentrations of the ions in the two different stages of oxidation, rather than on the actual concentration of either ion. The potentials of different reducing agents vary according to the value of the ratio $\frac{\overline{R}}{\overline{R}}$, which can be maintained under the given conditions. For any actual concentration of $\overline{R}$, the concentration of $\overline{R}$ will assume a corresponding value, so that the reduction potential cannot be said to depend on the actual value of $\overline{R}$, *i.e.*, the dilution.

Consequently, if, on applying the method previously used

for determining the relative reducing energy, the energy should appear to fall off as the dilution is increased, we might conclude either that reduction potential and photographic reducing energy are not related, or that the bromide depression method is in error as a measure of the energy. If the reducing energy, however, does *not* vary with the dilution, the suggested explanation of the density-log dilution relation is at once eliminated and we have further evidence that the bromide depression method gives a measure of a fundamental characteristic of a developing agent.

Several experiments, first without, and then with, mechanical stirring, were carried out to establish this point. An elon developer (formula 7, p. 517) was used. 1½, ½ and 1/16 times this strength were employed. Density-time curves (extending up to an hour or more) were obtained for the above solutions. For the determination of the depression .01 M potassium bromide was used without stirring and 0.06 bromide in the experiment with mechanical stirring.

For the methods employed in studying these data, the reader is referred to previous publications cited. Density-gamma ($D-\gamma$) curves gave values of the density depressions, or amounts by which the density is lowered by the bromide. The reducing energy varies inversely with a function of the depression, that is, in general, the less the depression, the higher the relative energy.

The depression was also found by computing D_∞, or the maximum developable density, from the density-time curves by a method described in an earlier paper.[4] D_∞ is computed from the observed data by use of the equation $D = D_\infty (1 - e^{-k \log t/t_0})$. The lowering of D_∞ by the bromide is the depression.

It was interesting to ascertain if the more dilute developer was capable of developing as much density as the more concentrated one.[5] Table I gives results for two experiments on the values of D_∞ obtained without rapid stirring.

The figures show in every case not only that there is no decrease in maximum density with the more dilute solutions, but a small positive increase. It is therefore apparent that under the above conditions the dilute developer finally reduces more silver than the concentrated one. This probably occurs because of the effects of surface development and local exhaustion, as previously

[4] *Phot. J.*, Dec., 1920, pp. 285–286.

[5] "Theory of Development," p. 76 *et seq.*

indicated, which prevent the stronger solutions from doing their full work, and from possible hydrolysis effects which would give the dilute solutions the advantage as shown below.

Considering next the relative energies of the three solutions, Table II gives values of the density depressions determined by both the $D-\gamma$ and D_∞ methods.

TABLE I.

Values of D_∞. Three Concentrations of an Elon Developer.

	Original Set.		Second Set.	
	No Bromide.	0.1 M KBr.	No Bromide.	0.1 M KBr.
Conc. 1½	3.5	3.4	4.0	3.8
Conc. ½	4.2	4.0	4.3	4.1
Conc. 1/16	4.4	4.0	4.4	4.3

The results shown in Table II are in accord with those just considered, more weight being given to the $D-\gamma$ method than the maximum density (D_∞) method, as the former is more sensi-

TABLE II.

Values of Density Depression 0.1 M KBr. Three Concentrations of an Elon Developer.

	First Set.		Second Set.	
	$D-\gamma$ Method.	D_∞ Method.	$D-\gamma$ Method.	D_∞ Method.
Conc. 1½	.22	0.1	.20	0.2
Conc. ½	.14	0.2	.07	0.2
Conc. 1/16	.08	(0.4)	.05	0.1

tive and more accurate. The dilute solutions show less depression and therefore greater apparent energy.

However, with very rapid mechanical stirring as used by Sheppard and Elliot,[6] the results differed from those above. See Table III.

TABLE III.

Values of Density Depression. 0.06 M KBr. Three Concentrations of Elon Developer, with Rapid Mechanical Stirring D_∞ method.

Conc. 1½	0.22
Conc. ½	0.36
Conc. 1/16	0.51

[6] JOUR. FRANK. INST., 1923, p. 211. (The question of stirring is more fully discussed later.)

The maximum density method could not be applied as the dilute solutions, especially the 1/16 concentrations, on long development became rapidly oxidized because of vigorous stirring.

It is therefore concluded that under the latter conditions the dilute solutions deteriorate because of aerial oxidation, which is greatly accelerated by stirring. If there is any tendency for dilute solutions to show less relative energy, then the effect is masked by other factors when mechanical stirring is not used, as in the previous experiments. It seems far more probable that there is no change in relative developing energy but that the factors, surface tanning, local exhaustion, and aerial oxidation, are involved as indicated.

(6) Hydrolysis.

Before attempting to explain some chemical effects which may partially cause the results described, it is necessary to make certain assumptions. The task is difficult because so little information is available that nothing is known about the state of the solutions used and the effect of the various substances on each other. As hydroquinone is practically the only developer which has been even partially studied, we will confine our discussion more or less to a solution containing M/20 hydroquinone, and varying amounts of sodium hydroxide and sodium sulphite.

We assume first that the sulphite has no appreciable effect on the active constituent of the developer before development takes place, though it has an obvious effect on the dissociation of other sodium salts. Aside from its well-known soluble action on the silver halide, which is not of great magnitude, we assume that it does not materially alter the course of development.

There is insufficient evidence to discuss other possible conditions arising in development through the presence of sulphite. Among the most important contributions are those of Sheppard and Mees ("Investigations on the Theory of the Photographic Process," Longmans, London, 1907, p. 151; *Zeit. f. wiss. Phot.*, 2:7); Andresen (*Phot. Korr.*, 1900, p. 185); Lüppo-Cramer ("Eder's Jahrbuch," 1901, p. 44); Schilow and Fedotoff (*Zeit. f. Elektrochem.*, 1912, p. 928) and Luther and Leubner (*B. J.*, 1912, pp. 632 *et seq.*). It seems generally recognized that sulphite acts as a preservative by protecting the developer from oxidation and that it influences the density through its property of

partially dissolving the silver halides, but further than this opinions differ. Practically, in our own work, we found that considerable variation in sulphite content had little effect on the characteristics under investigation here and this fact made us skeptical of adopting as yet any definite view of the matter.

Previous work by Frary and Nietz (*J. Am. Chem. Soc.*, 1915, p. 2273) indicated that when a developer is made up of hydroquinone, sodium hydroxide (or other alkali) and sodium sulphite, the hydroquinone is partially neutralized by the alkali, the remainder of the developer combining with the sulphite. The matter has never been further investigated. Luther and Leubner (*loc. cit.*) found that the neutralization of hydroquinone proceeds with more or less rapidity according to the concentration of hydroxyl ions, in some cases a rather long time being required for the attainment of equilibrium. It may be possible that the unneutralized portion of the hydroquinone combines with the sulphite in amounts depending on the velocity of neutralization.

Nothing is known definitely concerning the possible reactions between hydroquinone and sulphite because as yet no quantitative methods are known which can be successfully applied to the problem. The formation of the sulphonic acid derivative appears doubtful under conditions here employed, high temperatures and concentrated sulphuric acid being necessary. During the present work, different methods of making up the developer were employed, and such slight differences in density were shown that it was concluded that the sulphite had not greatly influenced the state of the solution before development. In making up the developer by different methods (by varying the order in which the chemicals were dissolved, their relative concentrations, etc.), many marked color reactions were observed. Some of these have been commented upon by Luther and Leubner. No matter what the color of the resulting developer, however, the photographic differences were very slight indeed when the solutions were fresh. Time did not permit systematic investigation of the effect of sulphite, but a number of preliminary experiments were made.

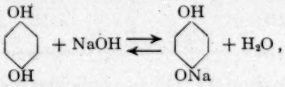
Those made during the present investigation (not described in detail here for lack of space) and earlier work [7] gave results not always consistent but showing in general that the developed

[7] A. H. NIETZ, "The Theory of Development."

photographic density was not affected over a wide range of sulphite concentrations.

A careful comparison of sodium and potassium sulphites did not yield any useful conclusions. The isohydric depression of the ionization of the sodium phenolates formed could not be photographically detected, the hydroquinone showing no less activity in the presence of sodium sulphite than with the potassium salt.

Under these unsatisfactory conditions we will next investigate what part hydrolysis might play in the variations shown with dilution. In brief, the subject is considered because the ordinary developing agents unite with the alkali to form phenolates and these are believed to furnish the active constituent, which is the anion. Thus we have hydroquinone and sodium hydroxide reacting:



the photographically active anion formed in this case being

.

It is evident that the concentration of this active anion will depend on the degree of hydrolysis of the phenolate. As the latter changes with the dilution, the subject becomes of interest.

Most of the common developing agents in solution ready for use may be considered as salts of weak acids, which compounds, as a class, are hydrolyzed when dissolved in water.

The degree of hydrolysis depends on the ionization constants of the acid and base in question, and that of the water. Where these constants are known we can calculate the degree of hydrolysis, h, which is the fraction of the salt which has undergone hydrolysis. It is this we propose to do in a few simple cases.

The process of hydrolysis is exemplified by the reaction between sodium carbonate and water.

$$Na_2CO_3 + H_2O \longrightarrow NaOH + NaHCO_3 .$$

In general, expressed in more modern form, this reaction is

$$(\dot{B} + \bar{A}) + H_2O \rightleftarrows (\dot{B} + \bar{O}H) + HA .$$

For the weak electrolytes involved we have two equilibrium equations which must be satisfied.

$$\frac{[\overset{+}{H}]\ [\bar{A}]}{HA} = K_A . \qquad (1)$$

$$[\overset{+}{H}]\ [\overset{-}{OH}] = K_W , \qquad (2)$$

where K_A and K_W are the ionization constants of the weak acid and water, respectively. Taking the case of hydroquinone, we may have: If molecular ratio $\frac{NaOH}{Hydroquinone} = 1.0$.

$$C_6H_4\langle^{OH}_{OH} + NaOH \rightleftharpoons C_6H_4\langle^{OH}_{ONa} + H_2O . \qquad (3)$$

If molecular ratio $\frac{NaOH}{Hydroquinone} = 2.0$

$$C_6H_4\langle^{OH}_{OH} + 2\ NaOH \rightleftharpoons C_6H_4\langle^{ONa}_{ONa} + 2\ H_2O . \qquad (4)$$

The first case (equation 3) will be particularly examined. Looking back, equations (1) and (2) in this case become

$$\frac{[\overset{+}{H}]\left[C_6H_4\langle^{\overset{-}{O}}_{O}{}^{OH}\right]}{[C_6H_4(OH)_2]} = K_A \qquad K_A = 1.1 \times 10^{-10} \text{ at } 25° ,$$

$$[\overset{+}{H}]\ [\overset{-}{OH}] = K_W \qquad K_W = 1.0 \times 10^{-14} \text{ at } 25° .$$

Combining,

$$\frac{[\overset{-}{OH}]\ [C_6H_4(OH)_2]}{\left[C_6H_4\langle^{\overset{-}{O}}_{O}{}^{OH}\right]} = \frac{K_W}{K_A} . \qquad (5)$$

We can now derive a method of calculating h, the degree of hydrolysis, for the reaction

$$C_6H_4\langle^{OH}_{ONa} + H_2O \rightleftharpoons C_6H_4\langle^{OH}_{OH} + NaOH . \qquad (6)$$

C_s = total concentration of salt $C_6H_4\langle^{OH}_{ONa}$,

$hC_s = [C_6H_4(OH)_2] = [NaOH]$,

$\alpha_B hC_s = [\overset{-}{OH}]$, where α_B is the degree of ionization of the NaOH formed.

The concentration of $C_6H_4\overset{OH}{\underset{O}{<}}^{-}$ ions is regulated by the degree of ionization of the salt, which is α_s. The concentration of the salt actually present is the hydrolyzed portion $(1-h)C_s$. Hence the concentration of the active anion $C_6H_4\overset{OH}{\underset{O}{<}}^{-}$ is $\alpha_s(1-h)C_s$. Substituting these values in (5), we get

$$\frac{[\bar{O}H]\,[C_6H_4(OH)_2]}{\left[C_6H_4\overset{OH}{\underset{O}{<}}^{-}\right]} = \frac{(\alpha_B h C_s)\,h C_s}{\alpha_s(1-h)\,C_s} = \frac{\alpha_B h^2 C_s}{\alpha_s(1-h)} = \frac{K_W}{K_A}.$$

If we make the assumption $\alpha_B = \alpha_s$, which is approximately true,

$$\frac{h^2 C_s}{1-h} = K_W \qquad \frac{K_W}{K_A} = \frac{1.0 \times 10^{-14}}{1.1 \times 10^{-10}}, \text{ or approximately } 10^{-4} \text{ at } 25°.$$

Then we have $\frac{h^2 C_s}{1-h} = 10^{-4}$, from which

$$h = \frac{1}{100}\left(\sqrt{\frac{1}{C_s} + \frac{1}{4C_s^2 10^4}} - \frac{1}{2C_s 10^2}\right). \tag{7}$$

By calculating the value of h for $C_6H_4\overset{OH}{\underset{ONa}{<}}$ in this manner, we arrive at the values given below. We have of course assumed that $\alpha_B = \alpha_s$, that is, that the dissociation of the monophenolate is the same as that of NaOH, and further that the presence of the sulphite does not interfere. K_W and K_A have the values already mentioned. Normal or unit concentration is taken as M/20 (0.05 M) developing agent, and multiples of this are expressed in the first column.

TABLE IV.

Relative Conc. of Dev.	C_s.	h at 25°.
4	.20	.022
2	.10	.03
1	.05	.045
1/2	.025	.06
1/4	.0125	.086
1/8	.00625	.12
1/16	.00313	.16
1/32	.00156	.22
1/64	.00078	.30

It is seen that the degree of hydrolysis is very appreciable in the dilute solutions.

From what has just been said, it is now seen that the concentration of the active ion $C_6\bar{H}_4\begin{matrix}OH\\O\end{matrix}$ depends on the concentration of the salt $C_6H_4\begin{matrix}OH\\ONa\end{matrix}$, or C_s, which in turn depends on the hydrolysis reaction. The problem now is simply to determine the effect of the hydrolysis on the concentration of the active ion. To do this a comparison is made of the concentration of $C_6\bar{H}_4\begin{matrix}OH\\O\end{matrix}$ with C_s. It was previously shown that

$$\left[C_6\bar{H}_4\begin{matrix}OH\\O^-\end{matrix}\right] = \alpha_s (1 - h) C_s .$$

Hence

$$\frac{\left[C_6\bar{H}_4\begin{matrix}OH\\O^-\end{matrix}\right]}{C_s} = \alpha_s (1 - h) ,$$

which is the ratio we want.

α_s is assumed $= \alpha_B$ and the values of α for NaOH at 25° are taken from Frary and Nietz.[8] h is calculated as indicated by equation (6). A typical set of values is given in Table V.

TABLE V.

Conc. of $C_6\bar{H}_4\begin{matrix}OH\\O\end{matrix}$ *at 25° in Hydroquinone 0.05 M, NaOH 0.05 M,* K_2SO_3 *0.1 M.*

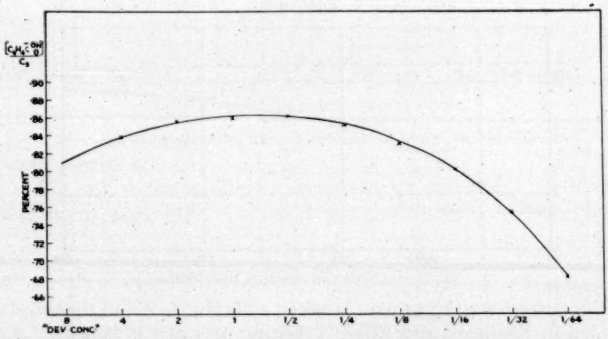
Relative Conc. of Dev.	C_s	h	α_s (= α_B for NaOH).	$\alpha_s (1 - h)$.
4	.20	.022	.858	.830
2	.10	.03	.882	.856
1	.05	.045	.90	.860
1/2	.025	.06	.917	.862
1/4	.0125	.086	.932	.852
1/8	.00625	.12	.944	.831
1/16	.00313	.16	.955	.802
1/32	.00156	.22	.966	.754
1/64	.00078	.30	.974	.680

[8] *J. Amer. Chem. Soc.* (1915) (*loc. cit.*).

Now we see at once, on looking at the last column, that the values of the ratio $\frac{\left[C_6H_4\begin{smallmatrix}OH\\O^-\end{smallmatrix}\right]^-}{C_s} = \alpha_s\ (1-h)$ rise to a maximum and then decrease. Plotted in the form of a curve, we have Fig. 13. Fig. 13, by coincidence, is practically identical with that for the phenolate of paraminophenol, $C_6H_4\begin{smallmatrix}NH_2\\ONa\end{smallmatrix}$ at 18°.

This curve and others for several developing agents computed in the same way, of course, suggest at once a possible

FIG. 13.



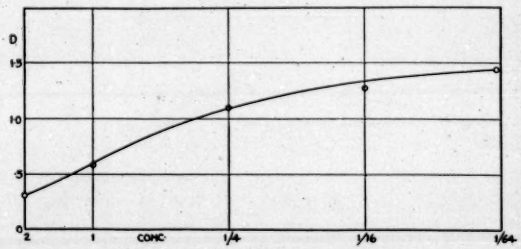
explanation for at least a portion of the falling off in density observed at high and low concentrations in the density-log *Dil* curves. After many calculations and attempts to straighten the *D*-log *Dil* curves by computing the "corrected" time of development, it was concluded that this effect accounted only partially for the decreases in density. This was especially verified after the experiments on stirring. That it is responsible for some of the effects noted seems very certain. A corresponding correction for the time of development increases the density at the high and the low concentrations with the result that the upward convexity of the curve is reduced.

(7) Effect of stirring.

We have considered the various possible causes of the abnormal effects of dilution in approximately their chronological order,

the order in which they were studied. After finding that hydrolysis did not wholly account for the results, we turned as a last resort to stirring, keeping in mind the results obtained by Sheppard and Elliott (JOUR. FRANK. INST., Feb., 1923, 211). An apparatus very similar to the one described by them (pp. 212–213, *loc. cit.*) was employed, the only difference being that radial baffle plates were inserted around the vertical walls of the developing chamber, and the films hung radially outside the stirring helix and cylinder. In this way eddy effects were absolutely prevented and films could be removed from the developer very quickly and independently of each other. The speed at which the

FIG. 14.



Dilution curve for elon developer with stirring.

helix turned was 200 r.p.m., a speed sufficient to avoid the effects noted by Sheppard and Elliott (shifting of *a* and *b* values). All films developed for the following series of experiments were stirred in this manner.

On determining some *D*-log *Dil* curves with stirring, it was found that with some developers the curve had a much different shape. Fig. 14 is such a curve for the developer:

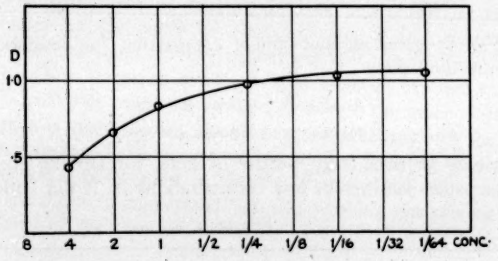
Elon $^{M}/_{20}$	NaOH $^{M}/_{20}$	Na_2SO_3 $^{M}/_{20}$
8.5 gm. per litre	2 gm. per litre	25.2 cm. per litre

On comparing with Fig. 7*A*, which is also for an elon developer, though not exactly the same, it is seen that there is not the falling off of density at the low concentrations there was when the solution was not stirred.

Fig. 15 is the curve for a paraminophenol developer stirred. The formula used was paraminophenol hydrochloride M/20

(7 gm. per litre) NaOH M/10 (4 gm. per litre) Na_2SO_3 M/5 (25.2 gm. per litre) and KBr (0.5 gm. per litre). Here again the first portion of the curve has something like the shape of those

FIG. 15.

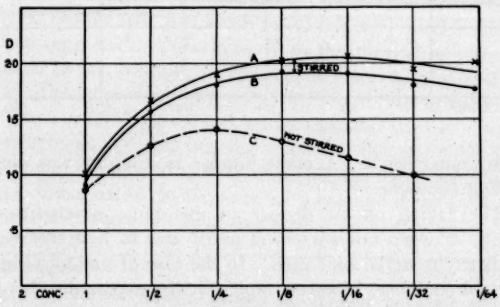


Dilution curve for p-a-p developer with stirring.

for the unstirred developers, but the density holds up for the weak solutions.

Fig. 16 shows a direct comparison of curves for unstirred and stirred solutions. Curves *A* and *B* are checks of each other

FIG. 16.



Stirred and unstirred developer. P-a-p.

for the stirred developer, while *C* is the result when the solution was not stirred. While many examples are not shown because of limited space, Fig. 16 is typical of nearly all the developers

tried, giving a fairly clear idea of how much stirring straightens the curve. The formula used was

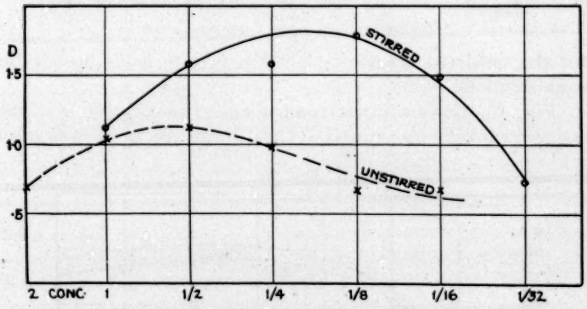
Paraminophenol	7 gm.
Na_2CO_3	50 gm.
Na_2SO_3	50 gm.
KBr	0.5 gm.

Fig. 17 gives another similar comparison for amidol. The formula used was

Amidol $M/_{20}$	8 gm. per litre,
Na_2SO_3	50 gm. per litre.

This case is particularly worthy of note, for stirring does not hold up the densities at low concentrations as it did with elon

FIG. 17.



Stirred and unstirred developer. Amidol.

or paraminophenol. A curve similar to Fig. 17 was obtained for hydroquinone.

The falling off of density in the dilute developers when stirred, as when not stirred, is partly due to hydrolysis effects and partly to aerial oxidation. In the case of amidol (Fig. 17) and hydroquinone, however, rapid stirring accelerates this aerial oxidation, as might be expected, because not only the oxygen already dissolved, but also the air churned into the solution becomes effective in rapidly oxidizing the developer. It is thus found that developers like elon and paraminophenol, which oxidize slowly, hold up well at great dilutions when stirred, showing

probably only the effect of hydrolysis. Developers like amidol and hydroquinone, on the other hand, oxidize quickly on standing, and stirring therefore causes an even more rapid decline in density at the low concentrations than would otherwise occur.

The real effect of stirring in this connection is partially explained by the paper of Sheppard and Elliott referred to. Uniform and rapid stirring washes out the bromide produced in the emulsion almost as quickly as it is formed. As this washing out is relatively more prompt and thorough, the more slowly the bromide is formed (*i.e.*, the slower the development) the more dilute solutions have the greatest advantage from the process and therefore show a gain in density, causing the curve at low concentrations to be elevated. In this washing out process other products of the reaction, including oxidized or spent developer, also disappear.

CONCLUSIONS.

The effects of dilution of photographic developers shown in curves 1 to 9, inclusive, are now thought to be caused by (in order of importance):

(1) The effect of hydrolysis in lowering the concentration of the active anion of the phenolate. This explanation breaks down for the amines, for which no satisfactory mechanism has yet been suggested. Unfortunately in the present investigation no amine, as for example, paraphenylene diamine, was used.[9]

(2) The imperfect outward diffusion of the bromide and other reaction products formed in the emulsion layer as development progresses. Proper stirring eliminates this effect and gives a differential increase of density, favoring the dilute solutions.

(3) Aerial oxidation accounts for a portion of the falling off in density with the more dilute solutions. This is, however, only a small amount and true practically only for developers which oxidize rapidly.

(4) Penetration effects caused by surface development and tanning not explained by 2. These conditions, if they exist, would affect only the concentrated solutions.

[9] Since this paper was written, a paper has appeared by Lüppo-Cramer (*Zeit. wiss. Phot.*, **24**, Feb., 1926, p. 13) in which he has found similar effects for various aminophenols and ascribes the results to hydrolysis.

On Wireless Interference Phenomena between Ground Waves and Waves Deviated by the Upper Atmosphere. E. V. APPLETON and M. A. F. BARNETT. (*Proc. Royal Soc.*, A764.)—The experimental evidence for the existence of the Kennelly-Heaviside layer is accumulating. This is an ionized stratum of the atmosphere high above the earth from which electrical waves are reflected. The authors of this paper in a previous communication related how they determined the angle of incidence of electrical waves assumed to be reflected from the layer, and interpreted their results "as yielding a direct experimental proof of the existence of the Kennelly-Heaviside layer, and also as demonstrating that the 'fading' of broadcasting signals at moderate distances from the transmitter was due mainly to interference phenomena between two sets of waves arriving at a receiver with an appreciable path difference." In the present paper they make use of another method published by them about two years ago. It is analogous to Lloyd's mirror interference system. Let light fall at almost grazing incidence on a horizontal mirror and after reflection proceed to a vertical screen, upon which is incident also light from the same source that arrives without having been reflected. The two rays falling on the screen have traversed different paths, and may, therefore, arrive in different phases. For one length of wave their effects will reinforce each other; for a different length they will be in opposition. Substitute for the source of light the sending station, for the mirror the layer in the upper air and for the screen the receiving station. In the experimental work a station near Peterborough received, while two sending stations were used at Bournemouth and at the National Physical Laboratory. The respective distances were 236 and 124 km. "Considerable difficulty has been experienced in finding a small wave-length range suitable for the experiment and free from interference by Continental broadcasting stations, which often transmit to 2 or 3 A.M." The wave-lengths employed were from 360 to 400 m. At the receiving station poorly selective amplifiers were made use of and photographic registration of the effect was obtained with an Einthoven galvanometer. A change of emitted wave-length was made uniformly during 5 secs., the change being 5 or 10 metres. All the 400 records taken show "the variation of the rectified signal current with time." Several reproductions of records are given. One pair was taken between the same stations and with the same original wave-length, but in one case the change was 5 m. and in the other twice as much. In the latter case the record shows twice as many maxima as does the former.

The authors interpret their observations as showing that the equivalent height of the reflecting layer rises gradually during the night only to sink rapidly about half an hour before sunrise. The reflected ray disappears altogether as the morning proceeds.

G. F. S.

A COMPARISON OF THE VARIATION OF INTENSITY AND DIRECTION OF RADIO SIGNALS.

BY

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THE marked development of the art of radio communication in the last few years has brought with it a growing interest in the phenomena of the change in direction of radio waves and fluctuation of signal intensity. Considerable experimenting has been done for long wave-lengths on transatlantic transmission, and recently several series of tests have been made under the direction of the Bureau of Standards of fading in the broadcast band. Very little work has been done, however, in comparing simultaneous records of direction and intensity fluctuation in the broadcast band or of simultaneous records of direction changes of signals from two or more stations. There is also need for further investigation of direction and intensity changes at the time of dawn or sunset, in the light of recent theory on the subject of the propagation of electromagnetic waves around the earth. It was for this reason that the experiments which form the basis of this paper were undertaken. It was particularly hoped that a study of simultaneous direction readings from two or more stations located in different directions from the receiving station would indicate whether or not an ionization gradient at the borderline between day and night causes a refraction of radio waves.

APPARATUS.

A considerable amount of time was spent in developing the apparatus used in the directional experiments. During the first tests made at Ithaca, N. Y., at the time of the total eclipse of 1925, it was found that a regenerative receiver employing one or two stages of audio-frequency amplification and preceded by a stage of tuned radio-frequency amplification was superior to a superheterodyne receiver. The reason for this was that the regenerative receiver could be allowed to oscillate and produce a very distinct heterodyne whistle whose intensity could be judged very much more accurately than modulated signals. Another advantage lay in the fact that it was possible to take readings

just as long as the carrier was strong enough to heterodyne the oscillating detector, even when speech and music were too faint to be distinguished. Two portable receivers of this type were therefore built and used in all later tests.

The first loop employed consisted of a solenoidal coil three feet square mounted so that it could be rotated about both a vertical and a horizontal axis. Very little directional variation about a horizontal axis could be detected, and due to the increased difficulty of taking data, no variations about a vertical axis were recorded throughout the tests. The loop was equipped with a scale graduated in degrees and was turned by grasping the frame about which the wire was wound.

It was soon found that this loop was unsatisfactory in several ways. It was necessary for the operator to stand up during the whole test, and due to the awkward method of turning it, it was impossible to take more than two readings per minute. It was also found to be almost impossible for one man both to set the loop and to record data. Another difficulty arose from body capacity to the loop, which at times produced such a variation of heterodyne frequency as to make it difficult to distinguish changes of intensity.

An attempt was then made to employ two large stationary loops mounted at right angles to each other and connected to two six-inch loops also mounted at right angles, within which was a rotating pick-up coil which connected to the receiver. This apparatus would undoubtedly be satisfactory if settings were made on modulated signals with a non-oscillating receiver, but the variation of capacity between the field coils and pick-up coil was found to produce too great a variation of the frequency of the heterodyne tone produced by the oscillating detector.

The set-up which was finally adopted consisted of a very light loop, two feet square, suspended by means of a ⅜″ brass road underneath a table large enough to hold another smaller table and a chair. The brass rod extended through the top of the upper table, and a dial calibrated in degrees was fastened to the end of it. The operator sat at the upper table and by means of the dial was able to rotate the loop quickly with one hand and record data with the other. On the edge of the upper table was mounted a telephone key-switch equivalent to two double-pole, double-throw switches, so that the phones and loop could be switched quickly

and simultaneously from one set to the other. A small flashlight lamp supplied light for night-time runs. With this apparatus it was possible for one man to take almost simultaneous readings on two stations at intervals of about fifteen seconds, and on one station about as often as they could be recorded. Very short leads connected the loop to terminals on the lower table. No difficulty was experienced in change of heterodyne frequency as the result either of variation of capacity between the flexible leads or to body capacity.

The apparatus used in making fading observations consisted of a three-stage superheterodyne receiver with a crystal rectifier and recording galvanometer connected in place of the second detector. A single-wire L-type antenna was used.

The fading apparatus was located in Rockefeller Hall of Cornell University throughout all the tests. Fading observations were made by Messrs. E. E. Zimmermann and C. W. Gartlein. During the August tests the directional apparatus was located in a barn on West Hill, about a mile and a half from Rockefeller Hall. During the December tests it was located in a wooden building at the Floricultural Experimental Station near Forest Home, about two and a half miles from Rockefeller Hall. Both of these locations were found to be sufficiently free from local disturbing influences, and average day-time directions from which the signals appeared to come corresponded with the true direction of the sending stations. Messrs. H. E. White, L. A. Wood, and F. W. Warburton assisted the writer in making direction observations.

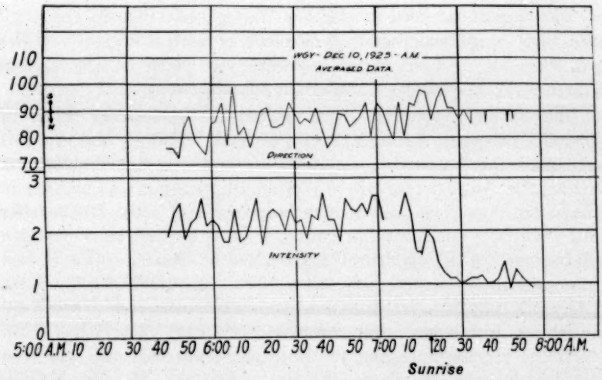
OBSERVATIONS AND TREATMENT OF DATA.

The directional settings recorded were those of minimum signal strength, which are very much sharper than the maxima. There was found to be little difference in the direction indicated by the two minima, and therefore only one setting was used. No attempt was made to check up on true and indicated average directions for every run, and as the tables were not rigidly fastened to the floor the true direction, indicated on the curves by means of a double arrow beside the scale of degrees, may be in error by two or three degrees.

For comparison of the various records, average data were obtained by measuring the area under the original intensity curves

for two-minute intervals by means of a planimeter, and by averaging the direction settings arithmetically over two-minute intervals. These data were used for plotting the average curves. In addition to this the actual intensity and direction curves were plotted on a common time base for a comparison of amplitude variations. Intensity ordinates are arbitrary. Direction ordinates are in degrees, but the zero ordinate is arbitrary as regards true north. The fading records made during August were not avail-

CURVE 1.



able at the time of construction of the curves here shown, and therefore comparison has been made only of direction charges for two stations. The latter data were taken with the original loop, and therefore not as many observations were recorded as might have been desirable.

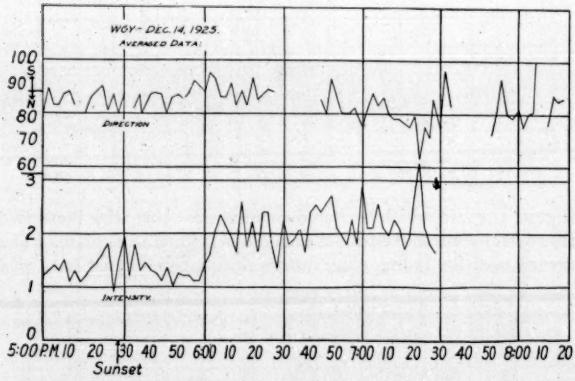
DISCUSSION OF OBSERVATIONS AND CURVES.

One of the first things that became apparent during the tests was that in general on nights when intensity changes were rapid and of large amplitude, changes of direction were also rapid and large. A number of times direction changes were so frequent and erratic that it was impossible to record data, or even to obtain accurate settings. On these nights fading showed the same characteristics.

Frequently the time of beginning and ending of night con-

ditions was practically simultaneous for intensity and direction changes, but this was by no means always true. Curve 1, for the morning of December 10th, shows distinctly the simultaneous return to daylight conditions. Data taken during the eclipse of January, 1925,[1] and in August, 1925, which are not available for publication in this paper, also showed a correlation in the arrival of night conditions for the two phenomena. Curve 4, for the evening of December 9th, fails, however, to show any such

CURVE 2.



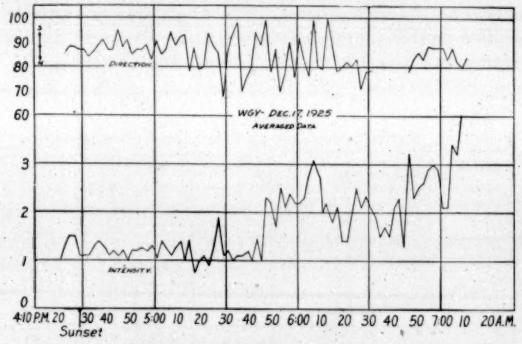
correspondence, and Curve 5 for December 17th shows that night conditions became pronounced at about 5 P.M. for direction and about 5.45 for intensity.

A careful comparison of average intensity and direction records for WGY on December 10th, 14th, and 17th (Curves 1, 2, and 3) fails to disclose anything but the purely chance correspondence which might be expected from two irregular curves of this type. It is possible to find a simultaneous occurrence of peaks and troughs, but it is evident that just as many times a peak in one curve corresponds to a trough in the other, or comes between a peak and a trough.

[1] ERNEST MERRITT, C. C. BIDWELL, and H. J. REICH: "Changes Observed in the Direction of Radio Signals at the Time of the Eclipse of January 24, 1925," JOUR. FRANK. INST., April, 1925.

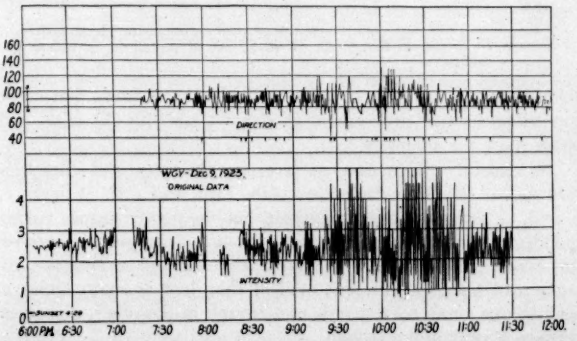
In the February, 1926, number of the JOURNAL OF THE FRANKLIN INSTITUTE, Prof. C. C. Bidwell presented a report of comparisons of direction and intensity variations observed during

CURVE 3.



August, 1925, in which he found correlation. Just why these two sets of data seem to contradict each other is hard to explain. The antenna used for fading observations during the August tests was

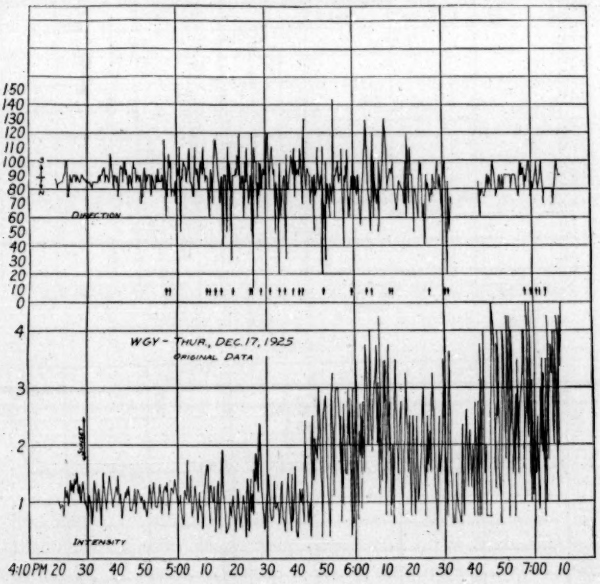
CURVE 4.



situated on the opposite side of the building from that used in December, and it is possible that absorption by the building caused the first antenna to be directional. If this were true we should

certainly expect to find a definite relation between intensity and direction changes. For the most satisfactory and convincing comparisons it would be necessary to locate the intensity recording apparatus out in the open, preferably within a few hundred feet of the directional apparatus. It is also possible that the dis-

CURVE 5.

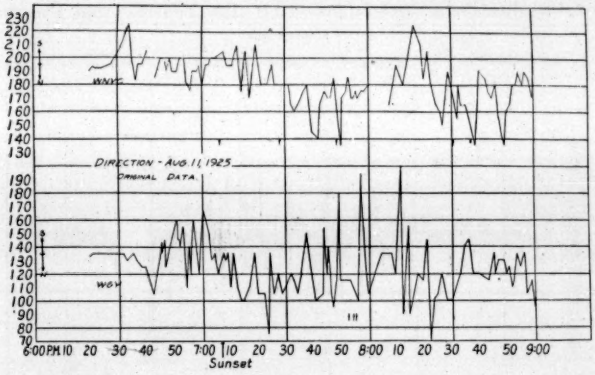


crepancy in the results of the two sets of tests was caused by a difference of weather conditions. A careful study of U. S. Weather Bureau records failed to disclose any clue in this direction, however.

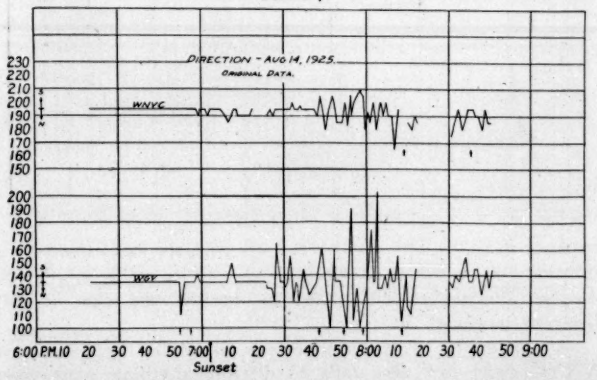
A comparison of direction records for WGY (379 m.) and WNYC (525 m.) also fails to disclose anything more than occasional chance correlation. On the evening of August 18, 1925, when direction changes were too erratic for recording continuous data, a comparison was made between the directions

of signals from WEAF (492 m.) and WNYC, both located in New York City. The difference of wave-length between these two stations is not great enough to give a very large difference of

CURVE 6.



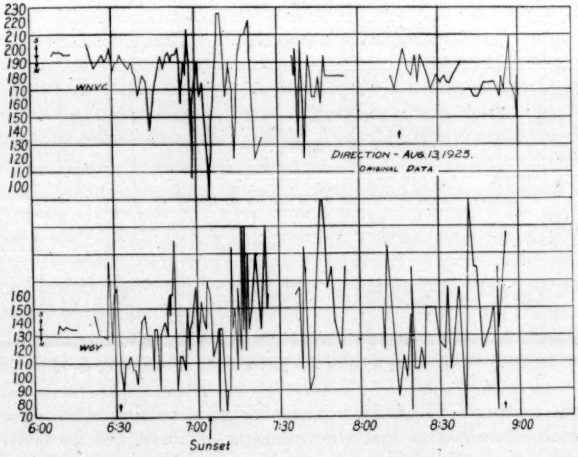
CURVE 7.



refraction of the sky waves from the two stations. The transfer from one station to the other could be made in the time taken to snap the key-switch, which was well within a quarter of a second.

To test for the minimum on the second station required not over two seconds. It was found that the settings for the two stations frequently differed by as much as thirty degrees. For a majority of these comparisons it was certain that for the elapsed time the rate of change of direction was not sufficient to account for such a large discrepancy. In fact, it was at times possible to shift several times from one station to the other before the readings changed.

CURVE 8.

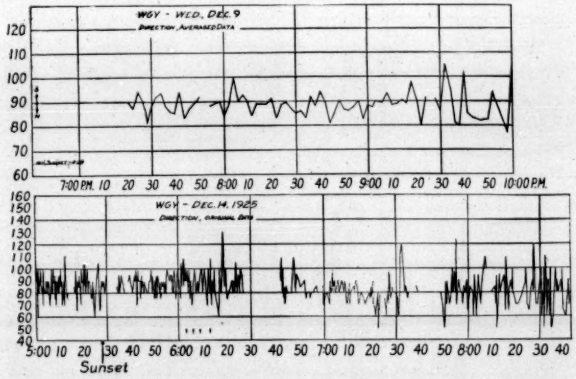


This seems to indicate that if changes of direction are due to reflection of the sky wave from some point in the Heaviside layer outside of the vertical plane containing the sending and receiving stations, the irregularities of the Heaviside layer which cause it must be small rather than large general distortions. If changes in direction are caused by a rotation of the plane of polarization, then even a very small difference in the speed of the two sky waves might result in different changes of direction such as were observed. However, the phenomena of fading and change of direction may readily depend either directly or indirectly upon so many factors that it does not seem surprising not to find a correlation.

A complete disappearance of direction has been indicated on the curves by means of vertical arrows.

On the evening of August 22d it was impossible to find directional minima for any station. After a time it was decided that something had gone wrong with the apparatus and the test was given up for the evening. A short time later it was discovered that there was a very strong display of the Aurora Borealis. Broadcast reception on an ordinary antenna was poor and erratic

CURVE 9.



that evening. The following evening good minima were again obtained, indicating that the apparatus was not out of order. Just how the Northern Lights could result in a complete absence of minima for all stations is a matter for further conjecture and experiment.

If the ionization gradient near the border between night and day did result in refraction, then it would be such as to bend the waves away from the sunlit hemisphere since their velocity would increase with the ionization. As the direction of WGY from Ithaca is approximately east-northeast, waves coming to Ithaca from this station would be bent toward the south at sunset. This would cause an apparent change of direction toward the north. Similarly, waves coming from WNYC in New York, which lies approximately southeast of Ithaca, would be bent toward the north and would appear to come from a point south of New York.

At sunrise these conditions would be reversed. Due to the persistence of ionization the deflection might be expected to come sometime after sunset.

Curve 9 for WGY on the evening of December 9th shows a slight deflection toward the north beginning about 7.30, reaching a maximum at 8.30, and ending at about 9. Curve 2 for the evening of December 14th fluctuates somewhat, but shows a decided deviation toward the north beginning at 6.45, and reaching a maximum at 7.20. The end of the record is not sufficiently accurate to indicate definitely the return to normal. Curve 3 for WGY on the evening of December 17th shows a deflection toward the north throughout the test, with a possible maximum at about 6.20. These results are rather encouraging, but an examination of the curves for the August tests makes the results appear to be a matter of chance or of local disturbances in the neighborhood of the receiving station. On the evening of August 11th (Curve 6) we have a deflection toward the north for both WNYC and WGY, reaching a maximum at about 7.50. On the evening of August 13th (Curve 8) we have a deflection toward the north for WNYC, reaching a maximum at 7.15 and to the south for WGY, reaching a maximum at 7.40. This is just the opposite of what we should expect. Curve 7 for the evening of August 14th shows a slight deflection toward the north for WNYC and no deflection for WGY. The deflection toward the north for WGY on the morning of December 10th (Curve 1) is also contrary to what would be expected.

CONCLUSIONS.

The results of these experiments lead to the following conclusions:

(1) Rapid and pronounced fading is usually accompanied by rapid direction changes of large amplitude throughout an evening, but there seems to be no correlation as to the exact time at which the changes occur for the two phenomena, or between the amplitudes of fluctuations over a short interval.

(2) The two phenomena frequently begin and end almost simultaneously, but not always.

(3) There is no correlation between direction changes in the signals from two different stations.

(4) Although there almost always seems to be a pronounced deflection of fairly long duration shortly after sunset and shortly before sunrise, this is not always in the right direction to verify the theory of refraction at the border between day and night.

(5) A display of the Northern Lights appears to result in an absence of directional minima on all stations.

If further tests of this sort are to be made in the future, it would doubtless be best to locate direction and fading apparatus at the same point, preferably in an open spot. Other observations taken during a display of the Northern Lights would be of particular interest. It is to be hoped that future experiments will help to clear up the seeming contradictions which have resulted from work which has already been done.

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THE DETONATION WAVE FROM SOLID EXPLOSIVES.*

BY

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DETONATION is a term that is commonly applied to the very sudden and rapid explosion of decomposable material, and, in the case of solid and liquid materials, to their almost instantaneous change into their gaseous combustion products. The velocity of detonation, under the influence of the proper initiating agent, is one of the highly significant properties of commercially important explosives of the dynamite type and a property that is carefully controlled.

The velocity of explosive materials within themselves has been studied with considerable exactness, because of its commercial importance. Means for controlling and altering the velocity of such materials have been known, but there has been little understanding of the underlying principles that determine the magnitude of the velocity. As to the behavior of the detonation wave after it leaves the explosive material, this has scarcely been investigated.

In connection with the prosecution of other work, an opportunity came to investigate the velocity of the detonation wave from dynamites in the interval beyond the explosive. That the detonation wave continues to travel beyond the limits of the explosive material is, of course, evident from the fact that the detonation of a mass of high explosive may be brought about by the explosion of another mass of high explosive when the two masses of material are separated by an inert medium such as an air-space. The effect produced is commonly known as explosion by influence or "sympathetic detonation." This property of explosives was early discussed at some length by Berthelot [1] and the whole subject of "Sympathetic Detonation" has more recently been reviewed by Storm.[2]

* Communicated by the Author.

[1] "Explosives and Their Power," translation, 1892.

[2] Army Ordnance, 1923, 3, p. 256.

In carrying out experiments on the velocity of the detonation wave in the medium immediately following the explosive, commercial dynamites were used in the form of cartridges, usually of 1¼-inch diameter. Two whole sticks of dynamite were used, in order that the velocity of the explosive should certainly reach its uniform maximum. The method of velocity measurement was the well-known Dautriche method,[3] which makes use of detonating fuse of uniform velocity, about 5000 metres per second, consisting of trinitrotoluene compressed into a lead tube of about ¼-inch diameter. In using this method for velocity measurements over an air-space beyond the explosive, the only variation from the ordinary was that the blasting cap at the first end of the detonating fuse was placed exactly at the end of the explosive cartridge. The other cap was spaced at the desired distance, pointing toward the explosive, with metal end cut off and mercury fulminate exposed, so that the detonation wave would be immediately detected. The explosive was wrapped in heavy paper, so that the column of paper extended slightly beyond the distance over which the velocity was to be measured.

VELOCITY OF DETONATION WAVE IN GASEOUS MEDIUM BEYOND EXPLOSIVE.

One would expect that, immediately beyond the end of the dynamite cartridge, there would be a falling off in the velocity of the detonation wave after the explosion. The surprising fact was met, however, that with certain explosives a considerable increase in velocity of the wave took place. This phenomenon is not altogether new, as Comey [4] and Laffitte [5] have each reported instances where somewhat higher velocities were obtained for the wave beyond the explosive than within the explosive.

Our early experiments showed that it was a usual thing for dynamites having a velocity in the vicinity of 2000–2500 metres per second to show an increased velocity of detonation wave in the medium following the explosive. In the case of dynamites of the ammonium nitrate permissible type having a velocity of around 2300 metres per second, the velocities through the gaseous medium over five- and ten-inch intervals were repeatedly found

[3] MARSHALL, "Explosives," 1917, **2**, p. 479.

[4] "Seventh International Congress of Applied Chemistry, 1909," Section IIIb, p. 35.

[5] *Comptes Rendus*, 1924, **178**, p. 1277.

to be 100 to 200 metres higher than the velocity of the explosive itself. A similar increase in the velocity in the air-space, of approximately the same magnitude, was found in the case of a 60 per cent. gelatine dynamite, having a velocity within itself of approximately 2400 metres per second. This increase in velocity did not take place, however, in the case of very high-velocity explosives, but instead a decrease was seen. Sixty per cent. straight dynamite, for example, with a velocity of 5800 metres per second, gave a velocity in air, in five- to ten-inch distances, of about 4400, while high-velocity 60 per cent. gelatine, with a velocity of 6400, showed a velocity in a similar air interval of about 4200. Beyond a distance of approximately ten inches, when cartridges of 1¼-inch diameter were used, the velocity of the detonation wave was found to fall off regularly.

UNIFORM VELOCITY ZONE.

Early indications had been that the velocity of the detonation wave over the first five inches beyond the explosive was the same as the velocity for ten inches, which would indicate a uniform velocity zone to a certain distance beyond the explosive, in which the velocity of the detonation wave was higher than the velocity of the detonation of the explosive. An ammonium nitrate permissible explosive was used, for example, which had the approximate composition of 10 per cent. nitroglycerin, 80 per cent. ammonium nitrate, and 10 per cent. of carbonaceous material similar to wood pulp. With this explosive, having a velocity itself of about 1960 metres per second, four determinations over distances of three to five inches had given an average velocity of 2164, while four other determinations over distances of six to ten inches had shown the average velocity of 2199. Similar results were obtained with 60 per cent. gelatin dynamite, of a velocity around 2400 metres per second. The average of five determinations over four- and five-inch intervals showed a wave velocity of 2678, while the average of six determinations for eight and ten inches was 2695.

A more careful check of the velocities of the detonation wave over the five-inch and the ten-inch intervals was made by selecting an ammonium nitrate permissible dynamite similar to the one used above, and having a velocity of about 2300 metres per second. Measurements of the velocity of the detonation wave were made

over a five-inch interval on ten successive shots, then over a ten-inch interval on ten shots. The results are shown below:

Distance.	Velocity.	Distance.	Velocity.
5″	2537	10″	2506
	2311		2350
	2337		2390
	2505		2403
	2505		2447
	2390		2377
	2390		2461
	2337		2521
	2447		2390
	2419		2362
	2418		2421

While there is considerable variation in individual measurements, there is an excellent average agreement between the determinations over the five- and ten-inch distances.

By the method used above, where the velocity of the detonation wave beyond the dynamite cartridge was measured, only one determination could be made on each shot. Since there is some variation in the velocity of different cartridges of the same dynamite, there would be even more significance to the results if measurements could be made of the velocity over different distances on the same shot. This was done by the use of a sphere of explosive. From large diameter cartridges of a 60 per cent. gelatin dynamite, it was possible to carve spheres of approximate exactness, four inches in diameter. The sphere was suspended in the air in a light cheesecloth bag so that the distance from the sphere to the ground was at least as great as the greatest distance through which the velocity was to be measured. The cap at the first end of the detonating fuse was fastened securely to the surface of the sphere with string, while the cap at the other end of the fuse, with exposed fulminate, was carefully spaced at the desired distance, and was pointed toward the sphere of explosive. The initiation of the explosive was by means of an electric detonator, whose charge was embedded as nearly as possible in the centre of the ball of explosive. The object of the experiment was to obtain further evidence of the existence of a zone of uniform velocity and to determine its extent.

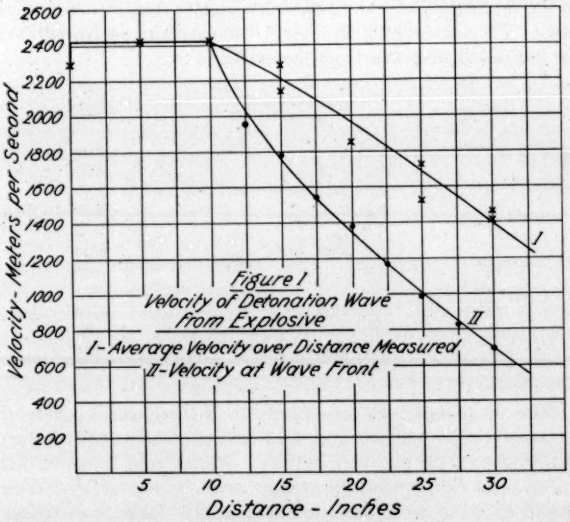
In the first shot, where velocities of the detonation wave were measured over distances of five and ten inches, good checks were obtained. In successive shots, the distances measured were increased until the limit of constant velocity was reached, each time one of the intervals measured being within the distances over which the velocity had been previously measured. Using this procedure, it was found that there was no decrease in the velocity of the detonation wave until distances greater than 25 inches were used. The tabulation below gives the velocities measured over the increasing distances from the explosive:

Distance.	Velocities Measured— Metres per Second.	Average Velocity.
5″	1930	1930
8″	2030	2030
10″	1870, 2250, 2080, 1980, 1960	2070
12″	2120	2120
14″	2180	2180
15″	2010, 2140, 1920	2020
16″	2030	2030
18″	2000	2000
20″	2140, 2250	2190
25″	1980	1980
26″	1740, 1790	1765
30″	1660	1660

The above tests very conclusively show that there is a zone of constant velocity and not a gradual falling off in velocity immediately beyond the explosive surface. In this case, however, the uniform velocity extends apparently to a distance of 25 inches, instead of about ten inches for the 1¼-inch diameter cartridge. It seems probable that the distances of uniform velocity are proportional to the diameters of the spheres of explosive detonated. In the case of cartridges of dynamite, the important consideration is the diameter of the cartridge, since the velocity of the detonation wave appears to be the same, regardless of whether a half stick or two sticks of dynamite are used. Hence, the sphere to be considered would be one having the same diameter as the cartridge. Since the distance of uniform velocity from the four-inch diameter sphere of explosive was found to be 25 inches from the surface of the sphere, the radius of the large sphere of uniform velocity would be 27 inches. The radius of a similar

sphere from a ball of explosive 1¼ inches in diameter, would be approximately 8.4 inches. In the case of the 1¼-inch cartridges, the dynamite was lying on the ground and the gases could not expand downward readily. Here it would be expected that the gas volume would be hemispherical rather than spherical. The radius of the sphere of influence therefore should be that of a

FIG. 1.



sphere having twice the volume of a sphere of 8.4-inch radius, or something over ten inches, which is the approximate limit for the zone of uniform velocity of the detonation wave, as determined with cartridges of 1¼-inch diameter.

BEHAVIOR OF DETONATION WAVE IN DISTANCE BEYOND UNIFORM VELOCITY ZONE.

Beyond the zone of uniform velocity, the velocity of the detonation wave from an explosive was found to decrease steadily. This is graphically shown in Fig. 1, where the velocity of the detonation wave from a 1¼-inch cartridge of an ammonium

nitrate permissible dynamite is plotted against the distance in inches. Two curves are shown, one for the average velocity of the detonation wave over the whole distance measured, the other for the velocity at the wave front. The velocities at the wave front are calculated from the averaged values on the other curve. The following tabulation gives values for the velocities at the wave front for three different dynamites:

Distance—Inches.	Ammonia Permissible Dynamite.*	60% Gelatin Dynamite.	60% Straight Dynamite.
0	2300	2400	5800
5	2420	2680	4400
10	2420	2680	4400
12.5	1970	2250	3810
15	1785	1875	3440
20	1380	1310	3000
25	990	880	2580
30	700	520	2160
35	....	....	1760
40	....	....	1420

*Approximate composition, 10 per cent. nitroglycerin, 80 per cent. ammonium nitrate, 10 per cent. carbonaceous material, *e.g.*, wood pulp.

THEORETICAL DISCUSSION.

Some very interesting suggestions may be drawn from the data presented above. In the first place, from the fact of the proof of the zone of uniform velocity, it is evident that the increase, or decrease, in velocity comes immediately after the detonation wave leaves the explosive. This in mediate change to a uniform velocity suggests that the cause may be the new medium into which the wave passes. A second suggestive feature is the fact that the velocity of the detonation wave falls off until it approaches the magnitude of the velocity of sound in air, a fact that arouses speculation as to whether the detonation wave may not be similar to a sound wave in its method of travel.

It is known that the velocity of sound increases with the temperature and that it is proportional to the square root of the absolute temperature, or $v_t = V_0\sqrt{(1+at)}$, where v_t is the velocity at $t°$ C. and a is the coefficient of expansion, or $1/273$. To explain a velocity of 2500 metres per second for sound would require the assumption of a temperature in the zone of uniform velocity of over 15,000° C., whereas the calculated temperatures

for commercial explosives have been in the neighborhood of 2000–3000° C. However, in calculating the maximum temperatures attainable with explosives, the temperatures have been arrived at thermochemically, by considering only the quantities of heat developed in the course of the reactions and the specific heats of the final products after combustion. No consideration has been given to the heating effect due to the enormous pressures developed at the time of explosion. If we could assume the explosive change from a solid to the great volume of gases to take place without loss of heat, as might seem permissible in view of the great velocity of the reaction, the change of temperature, due to compression of the gases into the originally occupied volume would be expressed by Rankine's formula: $\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$, in which T_1 and T_2 are the absolute temperatures before and after compression, V_1 and V_2 the volumes before and after compression, and γ the ratio of the specific heats at constant pressure and constant volume.

Dixon[6] has studied the velocities of explosion of gaseous mixtures, and has calculated the theoretical velocities of sound in the burnt gases by the above formula. He has then compared the calculated values with the measured velocities of explosion in the case of different gaseous mixtures. In the case of explosions of cyanogen with oxygen, for example, very close agreement was found between the calculated and measured values. For this reaction, $C_2N_2 + O_2 = 2CO + N_2$, Dixon obtained the calculated temperature of 21,190° (abs.), assuming adiabatic conditions.

Berthelot,[7] also, some years previous to Dixon's work, had measured the velocity of the explosion wave in gaseous reactions. Berthelot's theory was that the explosion did not travel with the velocity of sound in the hot gases, but with the velocity of propagation of the gaseous molecules themselves. The velocity of the gaseous molecules is calculated according to the formula of Clausius, where $v = 29.354\sqrt{\frac{T}{D}}$, in which T represents the absolute temperature and d the density of the gases compared to air. According to Dixon, the velocity of the sound wave is to the velocity of the gaseous molecules as 0.688 to 1.0, a ratio that is derived theoretically.

[6] *Phil. Trans. Roy. Soc. London*, Series A, **184**, pp. 97–188 (1898).

[7] BERTHELOT, *l. c.*

While conditions are quite different in the case of solid explosives from those holding in the explosion of gaseous mixtures, there seems to be no reason to think that the heating effect due to the compression wave resulting from the explosion would be any the less real in the case of solid than of gaseous explosives, and the compression effect should be very much magnified. At the very beginning of the zone of uniform velocity, following the explosive cartridge, the same conditions should hold as in gaseous explosions.

In attempting to calculate theoretical velocities for the detonation wave, it was not known whether to assume it to travel with the velocity of sound or with the rate of propagation of the hot gases. The latter assumption appeared to be reasonable and to agree best with experimental results. The tabulation below shows the relation of calculated and measured velocities:

Explosive.	Velocity M./Sec.	Calc. Temp. °C.	Velocity of Detonation Wave. Measured.	Calculated.	Per Cent. Attainment.
Blasting gelatin	7150	41,000	6400	6180	103.5
60% gelatin dynamite					
High-velocity	6400	17,600	4200	4330	97.0
Low-velocity	2400	17,600	2600	4330	60.0
40% gelatin dynamite	5210	13,500	3460	3510	98.6
40% straight dynamite	4500	15,300	3740	3790	98.7
Ammonium nitrate permissible	2400	27,400	2560	5320	48.2
Picric acid (density, 1.7)	7560	42,000	6280	8200	76.6
Picric acid (density, 0.824)	4560	57,000	3700	7020	52.7

The surprising thing in the above tabulation is that the agreement is as good as it is, between measured and calculated values, considering the fact that the exact reactions of decomposition at the time of explosion are not known and that the temperatures assumed are in regions where gas laws and specific heats have not been studied. In the reactions, carbon has been assumed to burn only to carbon monoxide. For the explosives listed above, four out of eight show really excellent agreement between theory and fact. The divergence can readily be explained in the case of the low-velocity 60 per cent. gelatin, for this is the same explosive as the high-velocity 60 per cent. gelatin, the difference in velocity being caused by the primer used. It is interesting to note that this explosive, when detonating at its maximum

velocity, gives almost the theoretical velocity for the detonation wave, while the same explosive, with a lower velocity than its maximum, falls much below the calculated velocity of the detonation wave. The ammonium nitrate permissible dynamite, which falls considerably below theoretical attainment, is an explosive whose velocity is probably much less than its maximum. This explosive contains about 80 per cent. ammonium nitrate, and Kast [8] found the velocity of detonation of ammonium nitrate to be much below his calculated value, when comparing it with other explosives. Picric acid is an explosive that is quite deficient in oxygen, and for this reason its decomposition products are very uncertain. It is interesting to note that, in the case of picric acid, the percentage attainment of the calculated velocity approached 100 as the velocity was brought to its maximum by increasing the density.

It is very possible that the assumptions made in the calculations above are not all justified. The theory suggested, however, seems reasonable and offers an explanation of facts that are difficult to explain otherwise. It gives a reasonable explanation of the otherwise obscure behavior of the detonation wave, in increasing in velocity after leaving one explosive and decreasing in another case. If the calculated temperatures are attained, they must be only momentary, since the assumptions under which they are calculated are that the reactions taking place are so extremely rapid that no loss of heat takes place and that constant-volume conditions are approached. The velocities assumed are the velocities not in air, but in the combustion gases. At all events, it seems probable that, at the moment of detonation, temperatures are momentarily attained very much higher than the temperatures usually calculated.

If the velocity of the detonation wave is assumed to be either the velocity of sound or the kinetic velocity of the gaseous particles at the momentary high temperatures, the fact that there is a constant velocity zone would mean that a uniform temperature prevails over this zone. The calculated temperature would be the temperature at the edge of the explosive, and it would be expected to fall off as the distance from the explosive increases. While no satisfactory explanation can be suggested for the failure

[8] KAST, *Z. angew. chem.*, 1923, 36, p. 72.

to do this, the zone of uniform velocity may be the volume that the gases of combustion occupy, and various influences come in that might help in maintaining the temperature, such as progressive burning of the carbon monoxide first formed to carbon dioxide and decrease in the specific heats of the products per unit volume, as they become less dense.

SUMMARY.

It has been shown that the detonation wave from a solid explosive changes in velocity after leaving the explosive. In the case of some low-velocity explosives, *e.g.*, about 2400 metres per second, the velocity of the detonation wave increases by approximately 100–200 metres per second. With other high-velocity explosives, 5000–6000 m./sec., the velocity may decrease to around 4400 metres in some cases.

Careful measurements have shown that a zone of uniform velocity exists beyond the surface of the explosive, the dimensions of the zone depending on the diameter of the sphere of the explosive or the diameter of the cartridge detonated. In the case of a 1¼-inch dynamite cartridge, the zone of uniform velocity extended for about ten inches, while, with a sphere of explosive four inches in diameter, the zone extended for about 25 inches.

An explanation of the reason for the high velocity of the detonation wave in the gaseous medium is suggested, linking it up with either the velocity of sound at the temperatures prevailing or the kinetic velocity of the gaseous particles themselves, the latter explanation appearing to be more in accordance with the determined facts. Such an explanation implies the assumption of extremely high momentary temperatures at the wave front, in some cases of over 40,000° C. These extremely high temperatures are due partly to the heat of combustion of the explosive ingredients but more to the heating effect resulting from the enormous pressures developed at the moment of explosion, as previously applied by Berthelot and Dixon in the study of gaseous explosions. Adiabatic conditions are assumed in such calculations. With such an explanation, reasonable agreement between theory and fact is obtained for a number of explosives, and the discrepancies that exist are in cases where discrepancies might be expected.

A Simple Lecture Experiment Showing Internal Friction in a Gas. KARL PRZIBRAM. (*Phys. Zeit.*, Dec. 15, 1926.)—A square 30 mm. on a side is cut from sheet brass about 5 mm. thick. From this is removed symmetrically a square 20 mm. on a side, so that there remains a hollow square with a marginal width of 5 mm. It is well, however, to provide a projection for supporting the device in a clamp. On each of the four sides of the square and at its middle a hole is bored parallel to the sheet through the 5 mm. of brass forming the margin. A glass plate is cemented across each face of the hollow square so that a body of air $20 \times 20 \times 5$ mm. is enclosed. Let the square be put in a vertical plane with its upper and lower edges horizontal. Pass a stiff wire of such dimensions as to fit snugly through the two holes in the vertical sides of the frame. Run in air containing ammonia gas through the lowest hole and put a drop of hydrochloric acid in the upper hole, letting it hang there as far down as possible. Project the apparatus on a screen. Clouds of NH_4Cl stream down from the drop. Pull the wire a short distance through its supporting holes with a velocity great in comparison with the speed of fall of the cloud. The cloud appears to be pulled along by the motion of the wire even at some distance from it, though the distortion is less and less at greater distances from the wire. The effect is quite similar to that obtained by dragging a wire through a viscous liquid though in the gas it is the transmission of motion from layer to layer that is the cause. G. F. S.

A Direct Reading Apparatus for the Measurement of Magnetic Fields. G. DUPOUY. (*Comptes Rendus*, Feb. 14, 1927.)—The principle of the device is the following. A crystal rotating about a suitable axis is subject, when placed in a uniform magnetic field, to a couple proportional to the square of the directing field. The crystal turns until it reaches a position in which the torsion of a wire or spring is equal to the couple called forth by the field. For each strength of field there is a definite position of equilibrium.

In the concrete apparatus the crystal used was carbonate of iron, siderite. This has different magnetic susceptibilities in different directions. It is supported rigidly within a horizontal tube resting against a conical point at each end. To this tube is attached a pointer that turns in a vertical plane in front of a graduated scale. As it turns it meets the opposition of a spiral spring. The apparatus enables readings to be taken very quickly. As the crystal need be no larger than a cylinder 2.5 mm. in diameter and 3 mm. in length, it can be employed to examine a field point by point, provided the intensity be sufficient. An apparatus made with siderite is, unfortunately, subject to corrections for temperature changes, because the couple caused by the field decreases as the temperature rises. The author hopes to evade this difficulty by using along with the siderite a second crystal whose couple increases with temperature elevation.

Prof. A. Cotton testified to the utility of the instrument.

G. F. S.

NON-UNIFORM LUMPED ELECTRIC LINES: I. THE CONICAL LINE.

BY

STUART BALLANTINE.

Member of the Institute.

THE important properties of the periodic electric networks formed of recurrent sections, discovered by G. A. Campbell, have in recent years been made the subject of a comprehensive literature.[1] Several years ago, at the time of my introduction to these structures by the lectures of Prof. G. W. Pierce, it occurred to me that the theory might be considerably extended to include lumped lines in which the values of the sectional impedances varied progressively from section to section in accordance with some definite law. So far as I am aware nothing has been published in this field, so that the present series of papers outlining the elementary results of these old investigations may be of some interest.

The original purpose of the lumped electric line seems to have been the artificial representation of actual physical smooth lines, primarily for the increased facility of laboratory investigation. Later, when their remarkable properties as wave filters were discovered, a new chapter in their development commenced. As simulative structures it is necessary that the current and voltage amplitudes vary from section to section in the same way that these amplitudes vary with the distance in an actual line. In discussing the uniform line Kennelly points out (*loc. cit.*, pp. 69 to 77) that simulating lumped lines may be built up either of T or Π

[1] G. A. CAMPBELL, U. S. Pat. No. 1,227,113, and *Bell Tech. Jour.*, 1, November, 1922.

A. E. KENNELLY, "Artificial Electric Lines," McGraw-Hill, New York, 1917.

G. W. PIERCE, "Electric Oscillations and Electric Waves," Chap. 16, p. 285, McGraw-Hill, New York, 1920.

K. W. WAGNER, *Arch. f. El.*, 3, 315, 1915; **8**, 61, 1919; *Zeit. f. Tech. Phys.*, **2**, 297, 1921.

O. J. ZOBEL, *Bell Tech. Jour.*, **2**, 1, 1923.

K. S. JOHNSON, "Transmission Circuits for Telephonic Communication," Chaps. 16 and 17, Van Nostrand, New York, 1925.

sections, and in the case of the former the voltage and current amplitudes of the *conjugate* smooth line correspond with those at mid-series of the lumped sections, while in the Π line the correspondence is at mid-shunt. In general the conjugate smooth line is not invariant of the frequency, but for a limited range the match may be extended by the employment of mutual induction between adjacent series sections as demonstrated by Pierce.[2]

In extending the theory and methods of construction to the more general non-uniform line, it is possible to follow two different methods: We may adopt the simulative viewpoint as above described and build up a line of T or Π sections in which E and I will vary from section to section in the same way that they vary with distance in the analogous and conjugate smooth line, or we may construct the lumped line so that when it is smoothed by allowing the sectional impedances to diminish and the number of sections to increase without limit, it will correspond with certain smooth lines whose properties are easily investigated as solutions of familiar differential equations. In this way lines of the exponential, gamma, Bessel, etc., types may be devised in analogy with the corresponding smooth lines. The first line is *simulative* and *confluent*, the second *confluent* but not necessarily completely simulative.

In the first method we start with the solution for the smooth line and in it replace the distance x by the section number m. This guarantees *a priori* the existence of the conjugate smooth line. The problem then consists of finding a physical structure of impedances for which the difference equation of propagation has this solution. In the second method the general plan is to start with the differential equation for the smooth line and derive by a method of approximation the *related difference equation.* It then remains to choose the sectional impedances so that this difference equation applies to the lumped line, that is to say, to devise a physical network having this equation as a relation between the current or voltage amplitudes in contiguous sections.

Such lines will not in general be true simulative lines, and a conjugate smooth line may not exist. In the case of the conical line to be considered in the following paragraphs, if we start with the differential equation for the current (I), the solution I for the lumped line may be similar to that for the smooth line, but the

[2] G. W. PIERCE, *Proc. Amer. Acad.*, **57**, 195, 1922.

transverse voltage will not correspond to the voltage in the smooth line nor satisfy the difference equation for E which is derived from the differential equation for E in the smooth line. Such a line is semi-simulative, being simulative only with respect to the current. Similarly it may be possible to start with the difference equation for E and derive a lumped line which simulates E rather than I, and in this case the currents may not correspond. This will suggest the wide variety of the possible ways in which the theory may be extended and also indicate the comparative simplicity of the uniform lines.

The present paper deals in an elementary way with the simplest of the non-uniform lines—the *conical line*—which as a member of the Bessel family is designated as of order ½. The development will first take the second of the above discussed paths aiming at a semi-simulative confluent line with respect to the current.

1. **Steady State Equations for the Smooth Non-uniform Electric Line.**—The transverse voltage and series current of an electric line having series impedance Z_1 and shunt impedance Z_2 (per unit length) are related as follows:

$$\left.\begin{aligned} \frac{dE}{dx} &= -(R_1 + i\omega L_1)I = -Z_1 I; \\ \frac{dI}{dx} &= -\frac{E}{R_2 + \frac{1}{i\omega C_2}} = -\frac{E}{Z_2}. \end{aligned}\right\} \tag{1}$$

This represents the steady state in which the effects vary with time as $Exp\ i\omega t$. Z_1 and Z_2 are functions of x. By differentiation and elimination between the above equations, the equations of propagation are derived as follows:

$$\frac{d^2E}{dx^2} - \frac{1}{Z_1}\frac{dZ_1}{dx}\frac{dE}{dx} - \frac{Z_1}{Z_2}E = 0, \tag{2}$$

$$\frac{d^2I}{dx^2} + \frac{1}{Z_2}\frac{dZ_2}{dx}\frac{dI}{dx} - \frac{Z_1}{Z_2}I = 0. \tag{3}$$

It will be convenient to consider the current as given by (3); E may be derived from I by (1).

Z_1 and Z_2 may be chosen as arbitrary functions of x. In deriving simple structures it is convenient to have Z_1 and Z_2 so

related that their ratio is independent of x and can be denoted by a constant propagation factor K^2. This is obviously by no means necessary and many interesting and solvable cases can be built up by allowing this factor to be a function of x. If this ratio is independent of the frequency, in addition to being independent of x, the structure is known as a *constant-K structure;* if it is merely independent of the frequency, it may be called a *frequency constant-K structure;* if independent of x only, it may be called a *space constant-K structure.*

2. Equation of Propagation for the Smooth Bessel Line.—The conical line is a special case of the Bessel line in which the impedances of the space constant-K line vary as a simple power of the distance x from the origin of the line:

$$\left.\begin{aligned} Z_1 &= z_1 x^n; \\ Z_2 &= z_2 x^n. \end{aligned}\right\} \text{(Bessel line)}. \tag{4}$$

Substitution in (2) and (3) leads to the equations:

$$\begin{aligned} \frac{d^2I}{dx^2} + \frac{n}{x}\frac{dI}{dx} - \frac{z_1}{z_2} I &= 0; \\ \frac{d^2E}{dx^2} - \frac{n}{x}\frac{dE}{dx} - \frac{z_1}{z_2} E &= 0; \end{aligned} \tag{5}$$

the first of which has the same *normal form* as the general Bessel equation and can therefore be transformed into it. The substitution is $I = x^{\frac{n-1}{2}} U(x)$. The function $U(x)$ satisfies the Bessel equation of order $\frac{n-1}{2}$, so that the corresponding line is described as of this order. The theory of this line was given by Heaviside (*vide,* "Electromagnetic Theory," Vol. 2, p. 238); I have considered the corresponding acoustic conduit in a contemporaneous publication.[3] The present term "conical" may appear somewhat fantastic as applied to the electrical line. It is suggested by the fact that in the analogous acoustic case the geometrical figure of the conduit is that popularly referred to as a "cone."

3. Smooth Conical Electric Line.—The smooth conical line is obtained by letting $n = \pm 2$. Two cases are distinguished accord-

[3] "On the Propagation of Sound in the General Bessel Horn of Infinite Length," JOUR. FRANK. INST., **203**, 85, January, 1927.

ing to the sign of the exponent. If positive the series impedance increases with x and the line will be called a *positive line*, and

$$\left.\begin{aligned} Z_1 &= z_1 x^2 \\ Z_2 &= z_2 x^2 \end{aligned}\right\} \text{ (positive conical line).} \tag{6}$$

If the sign is negative, the line will be referred to as a *negative line* and the impedances will vary according to the law:

$$\left.\begin{aligned} Z_1 &= z_1 x^{-2} \\ Z_2 &= z_2 x^{-2} \end{aligned}\right\} \text{ (negative conical line).} \tag{7}$$

It is convenient to choose for solution the differential equation, (2) or (3), which has its second term positive. We will thus consider the current I in the case of the positive line, and the voltage E in the case of the negative line.

Case 1: Positive Conical Line, $n = 2$.—The solution of (5) for this case is simply:

$$I = A\frac{e^{kx}}{x} + B\frac{e^{-kx}}{x}, \tag{8}$$

where $k = \sqrt{\frac{z_1}{z_2}}$. The equations describing the propagation in this line will be useful later for comparison with the corresponding equations for the lumped structure and may be briefly assembled.

The line will be considered as terminated at the distant end $x = l$ by an impedance Z_T and at the sending end, $x = a$, by means of an impedance Z_0 in series with the impressed e.m.f. of amplitude E_0. (Fig. 1.)

In the case of the *uniform* line the reflection coefficient at the termination of the line by an impedance Z is given by:

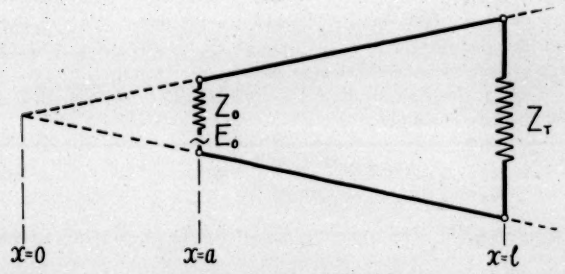
$$R = \frac{Z_i - Z}{Z_i + Z}, \tag{9}$$

where Z_i is the *characteristic impedance* of the line, $Z_i = \sqrt{z_1 z_2}$. In the case of the *non-uniform* line, Z_i is in general a function of x. It is, moreover, different for the two directions of propagation. I have found that in this more general case the reflection coefficient may be expressed as follows:

$$R = \frac{Z(\rightarrow) - Z}{Z(\leftarrow) + Z}. \tag{10}$$

Here $Z\ (\rightarrow)$ represents the characteristic impedance of the line for a wave approaching the terminating impedance and $Z\ (\leftarrow)$ is the characteristic impedance for a wave leaving the terminating impedance. The proof of this is easy and need not detain us, and the generalization may not be new. For the present line, in which the series impedance Z_1 varies as a positive power of the distance, $Z\ (\rightarrow)$ will be called the *direct (or outgoing) characteristic impedance* and is the impedance presented to a wave along the positive x axis; $Z\ (\leftarrow)$ will be designated as the *inverse (or*

FIG. 1.



Smooth positive conical line and terminations.

incoming) characteristic impedance corresponding to propagation in the reverse direction.

The characteristic impedance is defined as the ratio of E/I at any point, the line being considered as infinitely long. In the positive conical line:

$$E = Z_2 \frac{dI}{dx} = Bz_2 (1 + kx)\, e^{-kx} \text{ (outgoing wave)}, \quad (11)$$

$$E = Az_2 (1 - kx)\, e^{kx} \text{ (incoming wave)}; \quad (12)$$

so that:

$$Z (\rightarrow) = z_2 x + x^2 \sqrt{z_1 z_2}, \quad (13)$$

$$Z (\leftarrow) = -z_2 x + x^2 \sqrt{z_1 z_2}. \quad (14)$$

The latter impedance is obtained from the direct impedance by

simply changing the sign of x. The reflection coefficients are now found from (10). At the remote end of the line $(x = l)$:

$$Y = \frac{z_2 l\,(kl + 1) - Z_T}{z_2 l\,(kl - 1) + Z_T}, \tag{15}$$

and at the sending end $(x = a)$:

$$X = \frac{z_2 a\,(kl - 1) - Z_0}{z_2 a\,(kl + 1) + Z_0}. \tag{16}$$

The complete expression for the current amplitude I_x at any point x of the line can be readily found. The algebraic details need not be given. We find:

$$I_x = \frac{a}{x}\frac{E_0}{Z\,(\rightarrow)_a + Z_0}\frac{e^{-k(x-a)} + Ye^{-2kl}e^{k(x+a)}}{1 - XYe^{-2k(l-a)}} \tag{17}$$

where

$$Z\,(\rightarrow)_a = z_2 a + a^2\sqrt{z_1 z_2}, \quad k = \sqrt{\frac{z_1}{z_2}}.$$

This expression is very similar to that for the uniform smooth line, especially in respect to the interaction factor.

For an e.m.f. E_T applied at the high-impedance end of the line $(x = l)$, E_0 being absent, the current amplitude is given by

$$I_x = \frac{l}{x}\frac{E_T}{Z\,(\leftarrow)_e + Z_T}\frac{e^{-k(l-x)} + Xe^{2ka}e^{-k(l+x)}}{1 - XYe^{-2k(l-a)}}, \tag{18}$$

where

$$Z\,(\leftarrow)_e = z_2 l\,(kl - 1).$$

Case 2: Negative Conical Line, $n = -2$.—In this case the solution for E is:

$$E = A\frac{e^{kx}}{x} + B\frac{e^{-kx}}{x}, \tag{19}$$

from which I is derived through (1);

$$I = \frac{1}{z_1}[A\,(1 - kx)\,e^{kx} + B\,(1 + kx)\,e^{-kx}]. \tag{20}$$

For the characteristic impedances of the line, we have:

$$Z\,(\text{outgoing}) = \frac{z_1}{x + x^2\sqrt{\frac{z_1}{z_2}}}, \tag{21}$$

$$Z\,(\text{incoming}) = \frac{z_1}{-x + x^2\sqrt{\frac{z_1}{z_2}}}. \tag{22}$$

The reflection coefficients at the remote and near ends are, respectively:

$$Y = \frac{\frac{z_1}{l\,(kl+1)} - Z_T}{\frac{z_1}{l\,(kl-1)} + Z_T}, \tag{23}$$

$$X = \frac{\frac{z_1}{a\,(ka-1)} - Z_0}{\frac{z_1}{a\,(ka+1)} + Z_0}. \tag{24}$$

For the voltage and current amplitudes at a point x of the line, we have finally:

$$E_x = \frac{a}{x}\,\frac{E_0 Z\,(\text{out.})_a}{Z\,(\text{out.})_a + Z_0}\,\frac{e^{-k(x-a)} + Ye^{-2kl}e^{k(x+a)}}{1 - XYe^{-2k(l-a)}}; \tag{25}$$

$$I_x = \frac{E_0}{Z\,(\text{out.})_a + Z_0} \times \frac{\left(\frac{1+kx}{1+ka}\right)e^{-k(x-a)} + Y\left(\frac{1-kx}{1-ka}\right)e^{-2kl}e^{k(x+a)}}{(\text{same denominator})}. \tag{26}$$

4. Note on the Characteristic Impedances.—With reference to the positive line we see (equations 13 and 14) that in the case of a dissipationless line of impedances, $z_1 = i\omega L$ and $z_2 = 1/i\omega C$, the characteristic impedances are:

$$Z(\rightarrow) = \frac{x}{i\omega C} + x^2\sqrt{\frac{L}{C}}; \tag{27}$$

$$Z(\leftarrow) = -\frac{x}{i\omega C} + x^2\sqrt{\frac{L}{C}}. \tag{28}$$

The first is the impedance of a resistance and condenser in

series; the second that of a resistance and a *negative condenser* in series. Now a negative-capacity reactance in an electric circuit is an extremely rare thing; in fact, it is frequently said to be impossible of attainment in conservative passive networks. It is, therefore, of practical interest to examine the impedance of the inverted line in more detail to see if this structure is really capable of supplying this rare and desirable type of reactance.

The impedance in question (28) is obtained by inverting the line and having the source at $x = l$, the resultant wave travelling toward the origin to the left. The origin is a singular point of the differential equation; upon reaching this point, the wave is reflected back along positive x axis. It cannot be transmitted to the region of negative x because Z_1 becomes zero and short-circuits the line. In these circumstances the wave to the left is not suitably represented by Ae^{ikx}/x as assumed by (8), and the characteristic impedance derived from this expression is therefore not accurate when the line extends to the origin. The proper value of the impedance can be found as follows: Let the line be terminated for the moment at $x = a$ by an impedance Z_a and an e.m.f. E_T applied at $x = l$. Then the impedance of the terminated inverted line, looking toward the origin, is found from (18) to be:

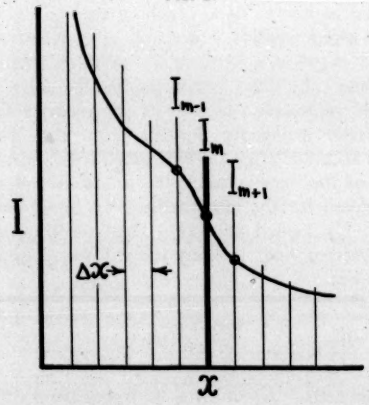
$$Z = \frac{E_T}{I_T} = Z(\leftarrow)_l \frac{1 - X\dfrac{Z(\rightarrow)_l}{Z(\leftarrow)_l} e^{-2k(l-a)}}{1 + Xe^{-2k(l-a)}} . \qquad (29)$$

X is given by (16). If now the X termination of the line is allowed to approach the origin by letting a approach zero, we see that unless the line is terminated unreflectively, that is unless $Z_a = Z(\leftarrow)_a$, X approaches $-i$. The line cannot be terminated unreflectively unless Z_a contains a negative capacity, hence this method of attaining $Z(\leftarrow)_l$ is impractical. It would seem that the correct impedance is given by letting $X = -1$ and $a = 0$ in (29), and the current by making the same substitutions in (18). Heaviside, in discussing the general Bessel line ("Electromagnetic Theory," Vol. 2, p. 258), considers original terminations and arrives at the conclusion that such constraints are impotent unless $1 > n > 1$. The conical line ($n = 2$) falls outside this region. It is concluded that the inverse characteristic impedance (28), exhibiting a negative capacity component, while perfectly legiti-

mate for use in the formulæ which have been given for the conical line terminated to the right of the origin, is not practically attainable in the steady state when the termination is removed and the line extends to the origin. This conclusion is also valid for the negative line.

5. Transition from the Smooth Line to the Analogous Lumped Line.—The related difference equations for the lumped lines are derived from the differential equations (5) as follows: The relations of the difference and differential equations have

FIG. 2.



been discussed by Richardson.[4] Let the interval $0-x$ be partitioned into m equal subintervals of norm Δx, such that $x=m\,\Delta x$. (Fig. 2.) Denote by I_m the current amplitude in the mth division. Then with the neglect of differential terms of higher order than the second, we have:

$$\frac{d^2I}{dx^2} = \frac{\left[\frac{dI}{dx}\right]_{m+1} - \left[\frac{dI}{dx}\right]_{m-1}}{2\,\Delta x} = \frac{I_{m+1} - 2I_m + I_{m-1}}{(\Delta x)^2}$$

$$\frac{dI}{dx} = \frac{I_{m+1} - I_{m-1}}{2\,\Delta x};$$

[4] RICHARDSON, *Bull. Amer. Math. Soc.*, December, 1919, p. 113, see also P. G. TAIT, Article "Waves," *Ency. Brit.*

so that when these approximate values are substituted in (3) there is obtained:

$$\frac{I_{m+1}-2I_m+I_{m-1}}{(\Delta x)^2}+\frac{n}{m\Delta x}\frac{I_{m+1}-I_{m-1}}{\Delta x}-\frac{z_1}{z_2}I_m=0. \quad (30)$$

Upon multiplying through by $(\Delta x)^2$ the last term becomes $\frac{z_1}{z_2}\Delta x^2$; $Z_1\Delta x$ is therefore taken as the total series impedance and $Z_2/\Delta x$ as the total shunt impedance of the mth section. These will be denoted by Z'_1 and Z'_2, respectively, and represent total series and shunt impedance elements. For a space constant-K system corresponding to the smooth line just considered their ratio remains invariant from section to section. We have then:

$$I_{m+1}\left(m+\frac{n}{2}\right)-mI_m\left(2+\frac{z'_1}{z'_2}\right)+I_{m-1}\left(m-\frac{n}{2}\right)=0, \quad (31)$$

as the difference equation for the current amplitude in the Bessel lumped line. The corresponding equation for the transverse voltage amplitudes is from (5):

$$E_{m+1}\left(m-\frac{n}{2}\right)-mE_m\left(2+\frac{z'_1}{z'_2}\right)+E_{m-1}\left(m+\frac{n}{2}\right)=0; \quad (32)$$

n is the exponent in the law of impedance variation.

6. Lumped Conical Line.—Reserving the discussion of the general solution of (31) for a second paper, we shall confine ourselves to the special case of the conical line furnished by $n=2$ as in Art. 3: (31) then becomes:

$$I_{m+1}(m+1)-I_m m\left(2+\frac{z'_1}{z'_2}\right)+I_{m-1}(m-1)=0, \quad (33)$$

of which the obvious trial solution is:

$$I_m=A\frac{e^{k'm}}{m}+B\frac{e^{-k'm}}{m}. \quad (34)$$

Substituting in (31), we find:

$$e^{k'}+e^{-k'}=2+\frac{z'_1}{z'_2} \quad (35)$$

or

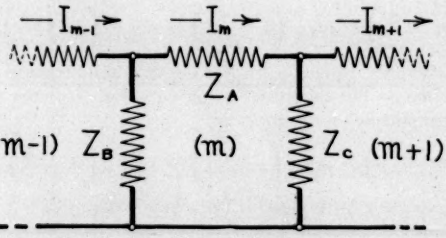
$$k'=\cosh^{-1}\left(1+\frac{z'_1}{2z'_2}\right)=2\sinh^{-1}\frac{1}{2}\sqrt{\frac{z'_1}{z'_2}};$$

k is the propagation factor per section. In the lumped line it is a

transcendental function of z'_1/z'_2, whereas in the smooth line it is absolutely equal to $\sqrt{z_1/z_2}$. This corresponds to the well-known filter action of the artificial line.

It is interesting to note that the determinantal equation (35) for k is precisely the same as that for the uniform or recurrent line. *This indicates that this conical line possesses the same filter and retardation properties as the more familiar recurrent lines.* These are well known and need not be discussed here except to note that in the interval: $0 > \frac{z'_1}{z'_2} > 4$ for real z'_1/z'_2, the attenuation is imaginary, giving no decrease in amplitude but a variation of

FIG. 3.



Section of lumped line.

the phase constant. Thus if $k' = A + i\Phi$, where A is the attenuation factor and Φ the phase factor:

$$\left.\begin{aligned} \sinh\frac{A}{2} &= 0, \\ \sin\frac{\Phi}{2} &= \frac{1}{2}\sqrt{\left|\frac{z'_1}{z'_2}\right|}. \end{aligned}\right\} 0 > \frac{z'_1}{z'_2} > 4$$

This represents the "transmitting band." In the attenuation band:

$$\left.\begin{aligned} \cosh\frac{A}{2} &= \frac{1}{2}\sqrt{\left|\frac{z'_1}{z'_2}\right|}, \\ \cos\frac{\Phi}{2} &= 0 \end{aligned}\right\} -4 > \frac{z'_1}{z'_2} > -\infty.$$

When z'_1/z'_2 is complex the determination of the attenuation and phase factors is more complicated. A very useful set of

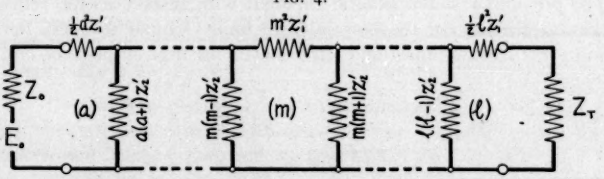
curves for these factors will be found in K. S. Johnson's "Transmission Circuits for Telephonic Communication" (Appendix E, pp. 294, 295).

7. Physical Structure of a Lumped Conical Line.—It remains to devise a physical structure such that (33) represents the relation between the current amplitudes in adjacent sections and in which the impedance elements vary from section to section in accordance with the general law for the conical line, viz., $Z = zx^2$. Consider the section of the network shown in Fig. 3. By a simple application of Kirchoff's laws it is found that the current amplitudes are related to the impedances in the following manner:

$$I_{m+1}Z_C - I_m(Z_A + Z_B + Z_C) + I_{m-1}Z_B = 0. \qquad (36)$$

Comparing this equation with (33) and letting $Z_A = z'_1 m^2$ where

FIG. 4.



Illustrating structure of positive lumped conical line and terminations.

z'_1 is the series impedance of the first section, we find that a possible section is obtained by letting:

$$\begin{aligned} Z_B &= m(m-1)z'_2; \\ Z_C &= m(m+1)z'_2. \end{aligned} \qquad (36b)$$

This structure is compatible in contiguous sections since $Z_C(m) = Z_B(m-1)$, and leads to the equation (33) for propagation.

8. Termination.—The lumped conical line just derived and its terminations are shown in Fig. 4. In the case of ordinary uniform lines it is customary to terminate the lines in a series element of impedance equal to one-half the series impedance of the section. It is found that this is the most convenient termination in the present case also. Therefore, inserting the impedances $\frac{1}{2}m^2z'_1$ in the ath and lth sections and following the method of Pierce in rendering the equations symmetrical for the terminal

sections, the following final results are obtained. All trivial algebraic details of their derivation have been omitted.

For the characteristic impedances:

$$Z(\rightarrow) = mz'_2 + m^2\sqrt{z'_1 z'_2}\sqrt{1 + \frac{z'_1}{4z'_2}}, \tag{37}$$

$$Z(\leftarrow) = -mz'_2 + m^2\sqrt{z'_1 z'_2}\sqrt{1 + \frac{z'_1}{4z'_2}}. \tag{38}$$

For the infinite line or one terminated in such a way that there is no reflection at the remote end, the impedance looking into the line from the ath section is:

$$Z(\rightarrow)_a = az'_2 + a_2\sqrt{z'_1 z'_2}\sqrt{1 + \frac{z'_1}{4z'_2}}. \tag{39}$$

The previously stated general theorem with respect to the reflection coefficients for the non-uniform line is found to apply here and gives for the reflection coefficients at the high-impedance end:

$$Y = \frac{l^2\sqrt{z'_1 z'_2}\sqrt{1 + \frac{z'_1}{4z'_2}} + lz'_2 - Z_T}{l^2\sqrt{z'_1 z'_2}\sqrt{1 + \frac{z'_1}{4z'_2}} - lz'_2 + Z_T}; \tag{40}$$

and at the low-impedance end:

$$X = \frac{a^2\sqrt{z'_1 z'_2}\sqrt{1 + \frac{z'_1}{4z'_2}} - az'_2 - Z_0}{a^2\sqrt{z'_1 z'_2}\sqrt{1 + \frac{z'_1}{4z'_2}} + az'_2 + Z_0}. \tag{41}$$

Finally for the complex current amplitude in the mth section we have:

$$I_m = \frac{E_0}{Z(\rightarrow)_a + Z_0}\frac{a}{m}\frac{e^{-k(m-a)} + Ye^{-k(2l-m-a)}}{1 - XYe^{-2k(l-a)}} \tag{42}$$

It remains to show that this line is simulative only as regards the current and that a completely conjugate smooth line does not exist. We first note that the voltage E_m between ground and a point in the middle of the series impedance of the section m may be derived from the solution (34) for I as follows:

$$E_m = \frac{1}{2} z'_2 m [(m-1)(I_{m-1} - I_m) + (m+1)(I_m - I_{m+1})] ; \quad (43)$$

$$= z'_2 [1 - m \sinh k'] e^{k'm} \quad \text{(incoming wave)}; \quad (44)$$

or

$$E_m = z'_2 [1 + m \sinh k'] e^{-k'm} \quad \text{(outgoing wave)}. \quad (45)$$

The E for the smooth line is from $(11) - z_2(1 \pm kx)e^{\mp kx}$, hence since $m \sinh k'm \neq km$ the E in the lumped line does not agree with that at a corresponding position angle on the smooth line. It is likewise easy to show that (44) and (45) do not satisfy the difference equation (32) for E, but are rather solutions of the difference equation:

$$E_{m+1}[1 + m(m-1)B] - 2E_m[B - 1 + m^2 B + (m^2 - 1)(B - 2)B] + E_{m-1}[1 + m(m+1)B] = 0 \quad (46)$$

wherein: $B = 2 + \frac{z'_1}{2z'_2}$.

9. **Comparison of the Lumped and Smooth Lines.**—Consider first the uniform line. The characteristic impedances of the smooth and lumped lines are as follows:

$$Z_i = \sqrt{z_1 z_2} = k z_2, \quad \text{(smooth uniform line)} \quad (47)$$

$$Z_i = \sqrt{z'_1 z'_2}\sqrt{1 + \frac{z'_1}{4z'_2}}. \quad \text{(lumped uniform line)} \quad (48)$$

In the case of the uniform line this impedance is iterative; it is also the same for propagation in either direction. In the conical line the outgoing characteristic impedances are:

$$Z(\rightarrow) = x z_2 + x^2 \sqrt{z_1 z_2}, \quad \text{(smooth conical line)} \quad (49)$$

$$Z(\rightarrow) = m z'_2 + m^2 \sqrt{z'_1 z'_2}\sqrt{1 + \frac{z'_1}{4z'_2}}. \quad \text{(lumped conical line)} \quad (50)$$

The analogy is apparent and supports the half-series termination for the conical lumped line.

The non-existence of the conjugate smooth line may also be inferred from these impedances. Denoting by z_1 and z_2, the constants of the smooth line (per unit length at $x = 1$), and by z'_1 and z'_2 those of the lumped line in the first section, for equality of position angles we must have $kx = k'm$, or

$$\cosh\sqrt{\frac{z_1}{z_2}} = 1 + \frac{z'_1}{2z'_2}, \tag{51}$$

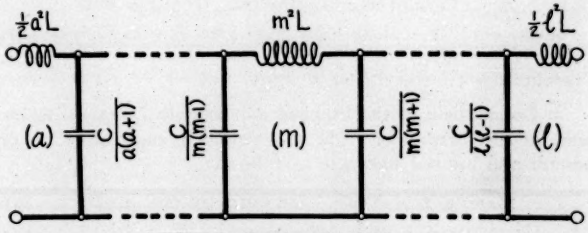
which determines the ratio z'_1/z'_2. For conjugacy between the lines the characteristic impedances at mid-series must agree at corresponding position angles for all values of m and x. This means that:

$$xz_2 + x^2\sqrt{z_1 z_2} = mz'_2 + m^2\sqrt{z'_1 z'_2}\sqrt{1 + \frac{z'_1}{4z'^2_2}}. \tag{52}$$

It is obviously not possible to choose z'_1 and z'_2 to satisfy (51) and (52) simultaneously.

10. **Special Cases.**—An idea of the performance of these lines may be obtained from the consideration of two simple cases:

FIG. 5.



Low-pass (L_1C_2) lumped conical line.

(a) The low-pass filter consisting of series inductance and shunt capacity elements, and (b) the high-pass filter having series capacity and shunt inductance. Both of the lines are assumed to be without dissipation.

Case a. Low-pass Filter.—The simple structure of the line is shown in Fig. 5. Here $Z_1 = i\omega Lm^2$; $Z_2 = \frac{m(m \pm 1)}{i\omega C}$, L and C being the constants of the first section. We have for the characteristic impedance:

$$Z(\rightarrow) = \frac{m}{i\omega C} + m^2\sqrt{\frac{L}{C}}\sqrt{1 - \left(\frac{\omega}{\omega_c}\right)^2}, \tag{53}$$

where ω_c is the cut-off angular frequency:

$$\omega_c = 2\sqrt{\frac{1}{LC}}. \tag{54}$$

In the transmitting band Z ($\rightarrow$) consists of a resistance and a capacitative reactance. The resistance component varies with ω/ω_c in the same manner as for the uniform line; the reactance component is, as we have seen, peculiar to the conical line.

In order to terminate the line non-reflectively at the high-impedance end, we must have:

$$Z_l = \frac{l}{i\omega C} + l^2\sqrt{\frac{L}{C}}\sqrt{1 - \left(\frac{\omega}{\omega_c}\right)^2}. \qquad (55)$$

The second term is a resistance and resembles the condition for non-reflection in the case of the uniform line. As in this case the variation of the line resistance with $\frac{\omega}{\omega_c}$ throughout the transmitting band does not permit the exact attainment of non-reflective output (or input) into a fixed terminal resistance. The condition will be approximately met over the greater part of the band if the terminal resistance is made approximately equal to the nominal characteristic impedance of the line, in this case $= \sqrt{L/C}$. If a more exact termination is desired, with greater frequency range of non-reflection, recourse may be had to terminations by half-sections of the m-derived types of three-element structure as suggested by Zobel,[5] m being usually selected to be about .6. Two such terminations are shown in Figs. 6*a* and 6*b*. Fig. 6*a* shows a mid-series section followed by an equivalent mid-series m-type half-section, which in turn has R_l as a mid-shunt termination. Fig. 6*b* shows a mid-shunt section with equivalent mid-shunt m-type half-section having R_l in mid-series termination. When applying these m-type terminating sections to the conical line a condenser of capacity C/l should be connected at X in Fig. 6*a*. If the m-type termination is omitted, we may make:

$$\left.\begin{aligned} R_l &= l^2\sqrt{\frac{L}{C}} \\ C_l &= \frac{C}{l} \end{aligned}\right\} \qquad (56)$$

The necessity for including a capacity of this value in Z_l may also be seen by considering the total impedance of the mid-shunt

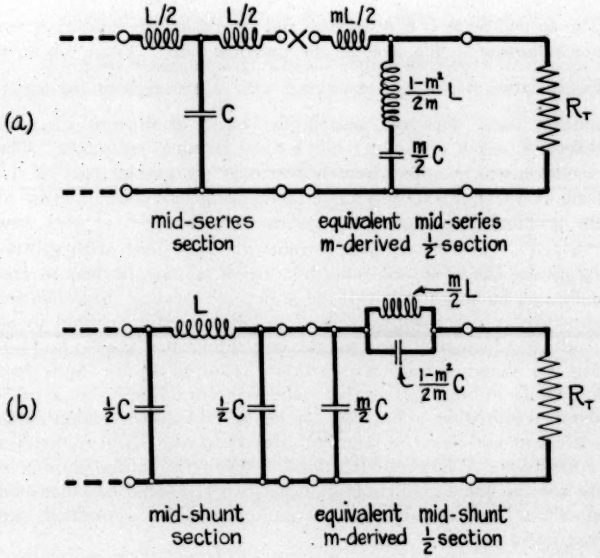
[5] ZOBEL, *loc. cit.*, p. 29.

section, which vanishes at the cut-off frequency in each section since this is a constant-K structure.

At the low-impedance end of the line we must have for non-reflection:

$$Z_0 = -\frac{a}{i\omega C} + a^2\sqrt{\frac{L}{C}}\sqrt{1-\left(\frac{\omega}{\omega_c}\right)^2}. \qquad (57)$$

FIG. 6.



(*a*) Terminations of mid-series section of lumped line by means of half-section of equivalent mid-series *m*-derived, constant-*K*, structure; (*b*) termination of mid-shunt section.

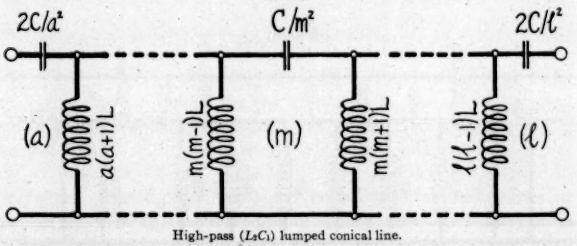
The resistance condition is readily fulfilled by the methods just discussed. The fulfilment of the second condition for the entire transmitting band demands that Z_0 contain a negative capacity reactance. The elimination of reflection at the low-impedance end of the conical line is practically impossible. The effect of this is readily seen. If an e.m.f. is operating at the low-impedance end

and there is no reflection at the high-impedance end, the current will be:

$$I_m = \frac{E_0}{Z(\rightarrow) + Z_0} \frac{a}{m} e^{-k(m-a)} \qquad (58)$$

The first factor represents the input-current into the line, the second represents the decrease in amplitude due to attenuation and to impedance variation. $Z(\rightarrow)$ contains a capacity reactance component, which, if not neutralized by Z_0, will limit the current entering the line at low frequencies. In this respect the electrical line emulates the analogous acoustic conduit, in which the propagation of the low-frequency vibrations is poor. The difficulty

FIG. 7.



High-pass (L_2C_1) lumped conical line.

of neutralizing the input capacity reactance of the conical line over the transmitting band would thus seem to constitute a decided limitation to the technical applications of this line.

Case b. High-pass Filter.—The structure and terminations of the high-pass filter are shown in Fig. 7. In this case $Z_1 = \frac{m^2}{i\omega C}$; $Z_2 = im(m \pm 1)\omega L$. The characteristic impedance now becomes:

$$Z(\rightarrow) = im\omega L + m^2 \sqrt{\frac{L}{C}} \sqrt{1 - \left(\frac{\omega_c}{\omega}\right)^2}, \qquad (59)$$

where ω_c is the cut-off frequency:

$$\omega_c = \frac{1}{2} \sqrt{\frac{1}{LC}}. \qquad (60)$$

Equation (59) shows that in order to terminate the line at the remote end without reflection, we must have:

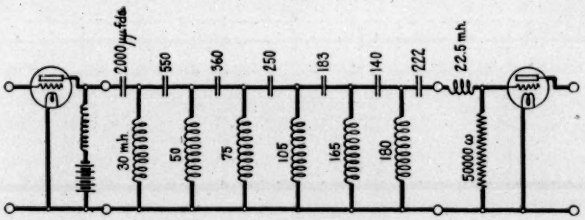
$$\left.\begin{aligned} R_T &= l^2\sqrt{\frac{L}{C}}\sqrt{1-\left(\frac{\omega_c}{\omega}\right)^2}, \\ X_T &= il\omega L. \end{aligned}\right\} \qquad (61)$$

In other words, in addition to the resistance R_T, we must add an inductance of value lL. At the sending end, elimination of reflection calls for:

$$\left.\begin{aligned} R_0 &= a^2\sqrt{\frac{L}{C}}\sqrt{1-\left(\frac{\omega_c}{\omega}\right)^2}, \\ X_0 &= -ia\omega L. \end{aligned}\right\} \qquad (62)$$

The reactance X_0 now required is that of a *negative inductance*,

FIG. 8.



Six-section high-pass conical lumped line between audion amplifiers.

which, like the negative capacity required for the low-pass filter, is not available practically.

11. **Example of Calculation and Application.**—The calculation of the constants of a simple conical filter may be illustrated by considering a practical application (Fig. 8). In Fig. 8 the high-pass filter L_2C_1 is shown as a connecting link between the tubes of an audion amplifier. The input resistance R_0 is the internal plate resistance of the tube, assumed to be 5000 ohms and the output resistance R_T, across which the second tube is connected, is taken to be equal to 50,000 ohms. For non-reflection the resistances must agree with the characteristic line impedances, thus:

$$R_T = l^2\sqrt{\frac{L_2}{C_1}} \quad \text{and} \quad R_0 = a^2\sqrt{\frac{L_2}{C_1}}, \qquad (63)$$

where a and l are the terminating section numbers. Taking the

ratio: $\sqrt{R_T/R_0} = l/a$. Let N denote the number of sections used; then $l = a + N$ and:

$$a = \frac{N}{\sqrt{\frac{R_T}{R_0} - 1}}, \tag{64}$$

from which to determine a and N, or a from N. In our case a is approximately equal to 3, so that if $N = 6$ sections then $a = 3$ and the six sections to be used will lie between 3 and 9. The inductance and capacity are related by the formula for the cut-off frequency:

$$LC = \frac{1}{4\omega_c^2}. \tag{65}$$

Then from (63)

$$C = \frac{a^2}{2\omega_c R_0} = .009 \text{ mfds.} \tag{66}$$

if $\omega_c = 1 \times 10^5 (\lambda = 19{,}000 \text{ m.})$, L is then found from (65) to be 2.5 millihenries. These are the values of C and L in the *first section;* their values for the sections from 3 to 9 (constituting the part of the filter to be used) are easily calculated from the law of variation (36*b*). The values so computed are marked in the figure. Finally the value of the terminating inductance at the output end is found to be $lL = 22.5$ mh. No attempt is made to reduce the reflection at the input end which arises from the inductive reactance of the line. The effect of this component of line impedance will be to limit the current at the higher frequencies. If this is undesirable some improvement may be effected by connecting a condenser in series or changing the value of the first series condenser so that this reactance will be neutralized at some particular frequency. Other impedance combinations may likewise be devised which will improve the transmission characteristic.

White Haven, Penna.
October 1, 1926.

LIST OF SYMBOLS.

E = Transverse voltage amplitude in smooth line.
I = Current amplitude in smooth line.
Z_1 = Series impedance per unit length at point x, smooth line.
Z_2 = Shunt impedance per unit length at point x, smooth line.
k = Propagation factor of smooth line = $\sqrt{z_1/z_2}$.
z_1 = Series impedance per unit length at $x = 1$, smooth line.

z_2 = Shunt impedance per unit length at $x = 1$, smooth line.
x = Distance along smooth line from origin.
n = Exponent in law of impedance variation in Bessel line.
Z_i = Characteristic impedance, uniform line.
$Z(\rightarrow) = Z(out.)$ = Characteristic impedance of non-uniform line for wave advancing from origin (left to right).
$Z(\leftarrow) = Z(in.)$ = Characteristic impedance of non-uniform line for wave approaching origin (right to left).
X = Reflection coefficient at sending end of line.
Y = Reflection coefficient at remote end of line.
I_m = Current amplitude (series) in the mth section of lumped line.
E_m = Voltage amplitude between mid-series and ground in mth section of lumped line.
Z'_1 = Series impedance in a section of lumped line.
Z'_2 = Shunt impedance in a section of lumped line.
z'_1 = Series impedance in first section of lumped line.
z'_2 = Shunt impedance in first section of lumped line.
m = Section number in lumped line.
k' = Propagation factor for lumped line.
ω = Angular velocity $= 2\pi \times$ frequency.
ω_c = Angular velocity corresponding to cut-off.

NOTES FROM LIGHTING RESEARCH LABORATORY, NATIONAL LAMP WORKS OF THE GENERAL ELECTRIC COMPANY.*

PROPORTIONS OF RED, GREEN AND BLUE IN SYNTHETIC WHITE LIGHT.

By A. H. Taylor.

PRACTICALLY any color of light, including white, can be produced by mixing red, green and blue light in varying proportions. The production of white by such mixtures is somewhat astonishing to anyone unfamiliar with the phenomenon. Furthermore, few if any of those familiar with it know the proportions of the different colors required to produce a good white or colorless light. Evidently the relative intensities of the different colors will depend on the saturation of the colors used.

Some tests have recently been made to produce white light by the use of available colored glass media used with gas-filled tungsten lamps. In the table below data are given for two combinations.

Relative Values of the Components of Approximately White Light, Produced by Mixing Red, Green and Blue.

Color.	Approximate Transmission of Colored Media.	Relative Proportions in White Light.	Relative Wattages of Clear Lamps Used with Colored Media.
	CASE I.		
Light red	19%	32%	5%
Dark green	3%	57%	63%
Dark blue	1%	11%	32%
	CASE II.		
Light red	19%	19%	5%
Strong yellow-green	11%	71%	32%
Dark blue	1%	10%	63%

Evidently this method of producing white light is very inefficient, as only 3 to 5 per cent. of the light from the clear lamp is utilized.

* Communicated by the Director.

VISION AS INFLUENCED BY A LIGHT-SOURCE IN THE FIELD OF VIEW.

By L. L. Holladay.

IT HAS been shown [1] that a light-source in the field of view causes an increase in the minimum perceptible brightness difference between an object and its background. On the assumption that this increase resulted from an increase in the adaptation brightness of the fovea it was found that the increase of adaptation was approximately proportional to the illumination at the eye from the light-source, and inversely proportional to the square of the angle between the line of vision and a line from the eye to the light-source.

The term "safety-factor of visual contrasts" has been proposed for the ratio between the actual contrast of brightness between an object and its background and the minimum perceptible brightness contrast under the conditions of adaptation existing at the instant of observation. Using this safety-factor as a measure of visibility, a study was made of the effect of a light-source, in the field of view, upon the visibility of a dark-gray object upon a light-gray background. If the light-source illuminated the eye but not the object, it was found that the visibility of the object was impaired, but less impaired the greater the initial brightness of the background. When the light-source was five degrees out of the line of vision and illuminated the eyes and background equally, it was found that the light-source aided vision only for very low initial brightnesses of background. When the light-source was five degrees out of the line of vision and the background had an initial brightness of 0.1 ml., it was found that for a constant safety-factor of ten (for any illumination from the light-source), its illumination upon the background must be 2.7 times its illumination at the eyes. Thus it was found that the ratio of illumination upon the background to its illumination at the eye must be greater than a definite minimum in order that it should aid instead of hinder vision. This minimum ratio of illuminations for non-interference of vision decreases as the angle between the line of vision and the light-source increases.

[1] Published in *Jour. Opt. Soc. Amer.* and *Rev. Sci. Inst.*, **14**, No. 1, p. 1, January, 1927.

THE RELATION BETWEEN EXTENT AND CONTRAST FOR THE THRESHOLD VISUAL STIMULUS.[2]

By P. W. Cobb and F. K. Moss.

THE sensitivity of vision may be measured in several ways. Perhaps the simplest is the use of the test-card of the ophthalmologist to determine the smallest letters which the subject is capable of reading. Another measure of visual sensitivity is used in photometry, in which the subject adjusts one part of a bright field until it matches the remainder as nearly as possible. In the first case the letters of the test-card stand in sharp contrast with the white card upon which they are printed and the measured quantity is the minimal size of letter recognizable. In the case of the photometer, the areas to be matched are gross, and the threshold difference in brightness is of importance.

These two forms of visual sensitivity are special cases at the extremes of a continuous series of possibilities and it is obvious that there must be some sort of complementary relationship between size of the object and brightness-difference when the object is at the threshold-point of visibility. Thus for each grade of contrast there is a threshold size of object and *vice versa*. The quantitative relation between these two has been determined, holding constant the other two variables of visual stimulus, namely, duration of exposure time and brightness level.

The experimental results gave a relation between contrast C (per cent. maximum) and size of object S (minutes visual angle) which can be expressed by the equation:

$$(C-a)\ (S-d)^m = b$$

in which a and d are values that C and S will approach asymptotically, and m and b are constants.

In the actual experiment, the exposure-time was held constant at 0.150 second and the brightness level at 20 millilamberts, and for these definite conditions, the constants in the equation:

$$(C-1.28)\ (S-0.56)^{1.399} = 13.97$$

were computed from the average of numerous results from nine subjects.

Adhesives and Adhesion. True Chemical Compounds as Adhesives. J. W. BAIN and W. B. LEE. (*Proc. Royal Soc.*, A765.)—"Adhesives are usually regarded as ill-defined substances

[2] To be published shortly in *Jour. Exper. Psych.*

of a colloidal nature, typified by glues, gums, resins, pastes and the like. It is the object of the present communication to show that pure substances can fully rival many of the common adhesives." This work is a part of an extended investigation of adhesives carried on by a committee of the Department of Scientific and Industrial Research. In an earlier report one of the authors working with a different collaborator stated that most common adhesives formed strong joints with metals. The strength of the joint reached two tons per square inch with shellac and its derivatives. They pointed out that true adhesion must occur when strong joints are formed with surfaces of polished metal or of optically polished silica or with true crystalline surfaces. There is no place here for the penetration of the adhesive into the pores or irregularities of the surface which leads to an effect simulating true adhesion.

The metal surfaces used were the fresh and carefully made, but not optically polished, ends of bolts. The two adhering surfaces were of the same material. The temperatures of the two metal pieces and of the adhesive originally in solid form were raised only a little above the melting temperature of the latter. A sliding motion brought the test pieces together in a manner to get rid of bubbles and unnecessary liquid. The two pieces were carefully aligned and let stand for some days, when the force needed to pull them apart was found. Among the substances investigated were benzophenone, salol, dextrose, Rochelle salt, cholesterol, T.N.T., and paraffin wax. As would be expected, the tension needed to pull the two surfaces apart depended both on the adhesive and on the metal. The force was usually between 100 and 1000 pounds per sq. in.

With optically plane surfaces the strength of the joint was measured when a liquid was between the ends. This amounted to only a few pounds per square inch.

The experiments indicate possibilities in the use of pure substances as adhesives that merit exploration. For example, between nickel surfaces the tension to break them apart when Rochelle salt was used was 1300 lbs./sq. in. while with marine glue it was the not much larger amount, 1550 lbs./sq. in. With regard to the thickness of the layer of adhesive the authors say, "We have been impressed with the importance of the rule 'the thinner the film, the stronger the joint.' This has been invariably substantiated whenever the film was still complete. It even extends to results obtained with liquids." It was also found that with the same adhesive in different states the joint strength was least with the liquid substance, greater with the substance crystallized and greatest with it in an amorphous form. This is in accord with the observation made in stressing pure metals that the fracture first comes, not at the irregular boundaries between the crystals, but across crystals. In many cases the strength of the joint was about the same, no matter whether tested by tension or by shear.

G. F. S.

NOTES FROM THE RESEARCH LABORATORY, EASTMAN KODAK COMPANY.*

PANCHROMATIC NEGATIVE FILM FOR MOTION PICTURES.[1]

By L. A. Jones and J. I. Crabtree.

THE first part of the paper deals with the fundamental physical and psychophysical relations which are fundamental to a thorough understanding of the rendition of the brightness of colored objects by the photographic process. The nature of radiation and light is discussed briefly. The meaning of the term "visibility of radiation" is defined and quantitative data relative to this function are given. The sensitivity of different photographic materials to radiations of different wave-lengths is discussed and illustrated by spectrograms and curves. The characteristics of light sources used in motion-picture work are discussed in detail and curves showing the spectral distribution of energy in the radiation from sunlight, skylight, tungsten lamps, arcs of various kinds, and the mercury-vapor lamps are given. One section deals with the nature of color, it being shown that the color of light is due to a spectral distribution of radiation different from that which is capable of exciting the gray sensation, while the color of non-luminous objects is due to the selective absorption of the radiation incident thereon. Examples are then given showing the difference between the rendition of brightness by orthochromatic and panchromatic motion-picture film. The advantages obtained by using panchromatic film in motion-picture work are outlined. These include the correct rendition of visual brightnesses, thus enabling the artist or cameraman to obtain with greater certainty the desired composition. The uncertainties and disagreeable appearance of present make-up methods are eliminated. The general atmosphere of the set has a greater semblance of naturalness and reality, etc. The use of panchromatic film, both regular and of special type, for such purposes as the

* Communicated by the Director.

[1] Communication No. 290 from the Research Laboratories of the Eastman Kodak Company and published in *Trans. Mot. Pict. Eng.*, 10, October, 1926, p. 131.

enhancement of brightness contrast, elimination of haze, obtaining moonlight effects, etc., is given. The last section of the paper deals with the handling of panchromatic film in the dark room. The questions of satisfactory safelights, dark room illumination levels, etc., are discussed.

IMPREGNATING WOOD WITH PARAFFIN.[2]

By L. W. Eberlin and A. M. Burgess.

SPRUCE impregnated with paraffin was found to withstand the action of acid and alkaline solutions with a minimum absorption of moisture and consequent swelling. The experimental work conducted to determine the most suitable kind of wood, impregnant, and method of impregnation is described. A practical method for the large-scale impregnation of spruce with paraffin is given. It was found that for the impregnation of wood with paraffin and similar substances the degree of impregnation was enhanced by the presence of 15 to 20 per cent. or more of moisture in the wood.

ON THE RELATION BETWEEN TIME AND INTENSITY IN PHOTOGRAPHIC EXPOSURE, V.[3]

By L. A. Jones, V. C. Hall, and R. M. Briggs.

THE effect of different developers and development times has been studied in detail. There is practically no difference in the curves of constant density for developers of widely different characteristics when development is carried out to the same point with each developer. A change in development time has no effect on the shape of the curves of constant density, but usually changes the position of optimal intensity. The results support the conclusions that the variation in sensitivity of individual silver halide grains with intensity follows a law similar to that of the whole emulsion, that all silver halide grains follow the same function, differing chiefly in the intensity for which the sensitivity is a maximum, and that at all intensities a grain is either entirely unaffected by the light falling on it or made completely developable.

[2] Communication No. 283 from the Laboratories of the Eastman Kodak Company and published in the *Ind. and Eng. Chem.*, 19, January, 1927, p. 87.

[3] Communication No. 292 from the Research Laboratories of the Eastman Kodak Company and published in *J. Opt. Soc. Amer.*, 14:223 (1927).

ON THE MEASUREMENT OF RESOLVING POWER OF PHOTOGRAPHIC MATERIALS.[1]

By O. Sandvik.

THE general practice among more recent workers in measuring the resolving power of photographic materials has been to photograph, in a reducing camera, on the particular material under consideration, some type of test-object. Much of this work has been done with a test-object consisting of a series of pairs of parallel lines the distance between the centres of which varied. The resolving power is defined to be numerically equal to the reciprocal of the distance, in millimetres, between the centres of the pair of lines just resolved. It has been assumed in some cases that only the periodicity, that is, the distance between the centres of the lines, and not the relative width of the lines to the separating opaque space was of importance. The present paper describes a new parallel line test-object whose ratio of width of the line to the space varied from 0.040 to 40.0. The results obtained with this test-object show a large variation in resolving power depending upon the value of the above ratio. For the range investigated, a linear relationship exists between the resolving power and the logarithm of this ratio.

The lack of agreement between the measurements made with the fan and the parallel line test-objects has been due, in part at least, to the fact that the ratio of the line to the space of the former was usually slightly less than unity while that of the latter was frequently much larger.

AN IMPROVED TYPE OF ILLUMINATION FOR USE IN METALLOGRAPHIC AND MINERALOGICAL MICROSCOPY.[2]

By L. E. Jewell.

THE paper describes an illuminator adapted for certain kind of microscopy. The novel features are a half prolate ellipsoidal hole in a stellite mirror, inclined at an angle of 45° to the microscopic axis, and a "nose piece" iris diaphragm. The light

[1] Communication No. 289 from the Research Laboratories of the Eastman Kodak Company and published in the *J. Opt. Soc. Amer.*, **14**, February, 1927, p. 169.

[2] Communication No. 291 from the Research Laboratories of the Eastman Kodak Company and published in the *J. Opt. Soc. Amer.*, **14**, February, 1927, p. 159.

coming from one side is reflected by the mirror down through one-half of the objective (except the central portions). The result is specular reflection from polished plane surfaces of the object which are perpendicular to the microscopic axis. This light passes back through the outer portions of the other half of the objective. This light irregularly or diffusely reflected from the object passes through the objective, and the hole in the mirror, as well as the unobstructed half of the objective, and gives a relief effect. The iris diaphragm limits the intensity of the specular reflection to any desired intensity. The nose piece diaphragm is also very useful where transparent objects are examined. The advantage of a wide-angled beam of light illuminating the structural detail of the object is retained. Illustrations show detailed plans of the illuminator and photomicrographs are given.

A PHOTOGRAPHIC METHOD OF SPECTROPHOTOMETRY IN THE RED AND INFRA-RED.*

By A. L. Schoen.

FOLLOWING the discovery of neocyanine, a new photographic sensitizing dye for the red and infra-red, photographic spectrophotometry in this region of the spectrum has been simplified considerably. Spectrophotometric apparatus consisting of a prism spectrograph, polarization photometer, and small "high intensity arc lamp" will be described. With this equipment the absorption curves for the Wratten light filters and several photographic sensitizing dyes have been measured from 500 to 900 mμ.

Potassium Xanthate as a Reagent.—IRVIN A. KOTEN (*Chemist-Analyst*, 1926, **48**, 6–7) recommends a 10 per cent. aqueous solution of potassium xanthate as a reagent for metals. It must be used in excess, and is of especial value when the metal forms several series of salts. Thus potassium xanthate yields a pale yellow precipitate with mercuric salts and a black precipitate with mercurous salts, a black precipitate with ferric salts and a light brown precipitate with ferrous salts, a greenish-yellow colloidal precipitate with ferricyanides and no change with ferrocyanides. J. S. H.

* Communication No. 293 from the Research Laboratories of the Eastman Kodak Company and published in *J. Opt. Soc. Amer.*, **14**, February, 1927, p. 179.

NOTES FROM THE U. S. BUREAU OF CHEMISTRY.*

THE PREPARATION OF CHLOROVANILLIN AND SOME OF ITS DERIVATIVES.[1]

By Raymond M. Hann and G. C. Spencer.

[ABSTRACT.]

A SEARCH of the available chemical literature having brought to light only a preliminary note on the preparation and properties of a chlorinated derivative of vanillin, the preparation and properties of chlorovanillin and some of its more common aldehyde derivatives were studied in the Bureau of Chemistry.

A method was devised for the preparation of chlorovanillin. The aldehyde is characterized by the preparation of the following derivatives: Oxime, hydrazone, phenylhydrazone, diphenylhydrazone, semicarbazide and thio-semicarbazide.

Condensation of chlorovanillin with cyano-acetic ester yielded ethyl-α-cyano-3-methoxy-4-hydroxy-5-chlorocinamate which, upon acid hydrolysis, gave the corresponding acid.

Schiff's bases were obtained by interaction of the aldehyde with aniline and β-naphthylamine.

THE PREPARATION OF ALIZARIN FROM PHTHALIC ANHYDRIDE AND ORTHO-DICHLOROBENZENE.[2]

By Max Phillips.

[ABSTRACT.]

THE synthesis of anthraquinone from phthalic anhydride and benzene, by the application of the Friedel and Crafts reaction, has of late become commercially important. This synthesis was made commercially feasible by the development in recent years of improved processes for the manufacture of phthalic anhydride and aluminum chloride. The applications of this synthesis are quite general, and a number of derivatives of anthraquinone are thus prepared commercially.

The Bureau of Chemistry has conducted a series of experi-

* Communicated by the Chief of the Bureau.

[1] Published in *Jour. Am. Chem. Soc.*, **49**, No. 2, pp. 535-537 (Feb., 1927).

[2] Published in *Jour. Am. Chem. Soc.*, **49**, No. 2, pp. 473-478 (Feb., 1927).

ments on the preparation of 2,3-dichloro-anthraquinone from phthalic anhydride and o-dichlorobenzene and on the conversion of the dichloro-anthraquinone into alizarin.

A synthesis of alizarin from phthalic anhydride and o-dichlorobenzene is brought about by the condensation of phthalic anhydride, o-dichlorobenzene and anhydrous aluminum chloride into 3′-4′-dichloro-2-benzoylbenzoic acid, and the conversion of this acid, by means of sulphuric acid, into 2,3-dichloro-anthraquinone. Upon fusion with alkali the dichloro-anthraquinone is converted into alizarin.

The claim of Sprent and Dodd that 2-chloro-anthraquinone is obtained by the condensation of phthalic anhydride and o-dichlorobenzene could not be confirmed.

THE SOLUTION PHENOMENA WITH VARIATION IN HYDROGEN-ION CONCENTRATION.[1]

By Walter C. Holmes and Julius F. T. Berliner.

[ABSTRACT.]

COMPARATIVELY little information is available in the literature respecting the behavior of aqueous solutions of dyes with variation in hydrogen-ion concentration. Limited data bearing upon indicator application have been collected and tabulated by Clark in his "Determination of Hydrogen Ions." Somewhat indefinite information on the behavior of dyes in general with acids and alkalies is also recorded in Schultz's "Farbstofftabellen" and in the more comprehensive tables of the "Colour Index of the Society of Dyers and Colourists."

The Bureau of Chemistry has outlined a system whereby the behavior of aqueous solutions of dyes with variation in concentration of hydrogen and hydroxyl ions is determined and recorded. The data obtained find their principal utility in the identification of dyes.

Atomic Weights.—The table of Atomic Weights, 1927 (*Jour. Am. Chem. Soc.*, 1927, **49**, 583–590) gives the following new values: Hafnium, 178.6; helium, 4.000; holmium, 163.5; lead, 207.22; titanium, 47.90; yttrium, 89.0; and zirconium, 91.22. The values for the other seventy-seven elements are unchanged. J. S. H.

[1] Published in *Am. Dyestuff Reporter*, **16**, No. 2, pp. 81–84 (Feb. 7, 1927).

THE FRANKLIN INSTITUTE.

(Proceedings of the Stated Monthly Meeting Held Wednesday, March 16, 1927.)

THE meeting was called to order at eight-nineteen P.M. by the President, Wm. C. L. Eglin. He announced that the minutes of the previous meeting had been printed in full in the March number of the JOURNAL of the Institute and that unless there were objection, they would be approved as printed. No objection was uttered and the minutes as printed were therefore declared approved.

The Secretary announced for the information of the meeting that since the February meeting eleven new members had been added to the enrolment, of whom seven were Resident, two were Non-Resident, and two were Student members.

He announced also, with regret, the death of one Resident member.

The President then introduced as the speaker of the evening, Dr. C. H. Kunsman, Physicist, the Bureau of Soils, U. S. Department of Agriculture, who read an important paper on "The Thermionic Emission from Iron Alkali Mixtures Used as Catalysts in the Synthesis of Ammonia." Doctor Kunsman talked especially of the work which had been done in the Bureau of Soils in the production of a surface catalyst. He told of important results which had been obtained through its use.

The paper of the evening was followed by a discussion, participated in by Prof. K. T. Compton, of Princeton University, and Prof. W. F. G. Swann, of Yale University. Professor Compton especially spoke in high appreciation of the importance of the work done by Doctor Kunsman.

The meeting was adjourned at nine-nine, by the President, with an expression of hearty thanks to Doctor Kunsman for his valuable paper.

HOWARD MCCLENAHAN,
Secretary.

COMMITTEE ON SCIENCE AND THE ARTS.

(Abstract of Proceedings of Stated Meeting Held Wednesday, March 2, 1927.)

HALL OF THE COMMITTEE,
PHILADELPHIA, March 2, 1927.

MR. M. M. PRICE, *in the Chair.*
Thirty-seven members present.

The following report was presented for final action:

No. 2865: Literature.

The Louis Edward Levy Medal to Dr. W. D. Coolidge, of the General Electric Company, Schenectady, N. Y., for his paper entitled "The Production of High-voltage Cathode

Rays Outside of the Generating Tube," appearing in the December, 1926, issue of the JOURNAL OF THE FRANKLIN INSTITUTE.

The following reports were presented for first reading:

No. 2834: Centrifugal Flotation Machine.

No. 2866: Brass Swing Check Valve.

GEORGE A. HOADLEY,
Secretary to Committee.

MEMBERSHIP NOTES.

ELECTIONS TO MEMBERSHIP.

(Stated Meeting, Board of Managers, March 9, 1927.)

RESIDENT.

MR. LOUIS B. BOND, Mechanical Engineer, Christiana Machine Company, Christiana, Penna.

MR. FRANCIS M. BROOKE, Banker, Fifteenth and Locust Streets, Philadelphia, Penna. For mailing: Bryn Mawr, Penna.

MR. GEORGE W. EATON, JR., Electrician, 1915 South Twelfth Street, Philadelphia, Penna.

MR. RUSSELL H. KENT, Mechanical Engineer and Executive, Clifton Heights, Penna.

MR. J. T. W. MARSHALL, Research, Victor Talking Machine Company, Camden, N. J. For mailing: 1718 Pine Street, Philadelphia, Penna.

MR. JOHN VANG. POSTLES, Assistant to Chief Engineer, Philadelphia Gas Works, 1401 Arch Street, Philadelphia, Penna.

DR. JOHN W. STOCKWELL, New Church Book Center, 2129 Chestnut Street, Philadelphia, Penna.

LIFE.

MR. THOMAS M. RECTOR, 5 Courier Street, Rutherford, N. J.

CONTRIBUTING.

MR. A. F. BABCOCK, Engineering Assistant, Traffic Department, Eastern Area, The Bell Telephone Company, 1631 Arch Street, Philadelphia, Penna.

DR. LEO BEHR, Research Engineer, Leeds and Northrup Company, 4901 Stenton Avenue, Philadelphia, Penna.

NON-RESIDENT.

MAJOR K. K. V. CASEY, Director of Sales-Smokeless Powder, E. I. duPont de Nemours and Company, Wilmington, Del. For mailing: 5060 duPont Building, Wilmington, Del.

MR. ALEXANDER C. VOGT, Chemical Engineer, National Fire Protection Association, 85 John Street, New York City, N. Y. For mailing: 255 Hicks Street, Brooklyn, N. Y.

STUDENT.

MR. GLENDEN J. DUNLAP, Student, Northeast High School, Philadelphia, Penna. For mailing: 3224 North Seventh Street, Philadelphia, Penna.

MR. S. MILTON RAMBO, Student, 406 Linden Street, Camden, N. J.

CHANGES OF ADDRESS.

DR. EDWARD G. ACHESON, 689 Fifth Avenue, New York City, N. Y.

MR. GEORGE W. BIRCH, JR., 7427 Bond Avenue, Upper Darby, Penna.

PROF. JOHN J. CATON, University of Detroit, Detroit, Mich.

MR. JOHN W. HORNSEY, 2 Whitehall Court, London, S. W. 1, England.

MR. BARTRAM A. OWEN, 802 Weightman Building, 1524 Chestnut Street, Philadelphia, Penna.

MR. LOUIS A. PARSONS, 394 First Street, Walla Walla, Wash.

MR. W. S. SLOATMAN, Supervisor, Reading Company, Mahanoy Plane, Penna.

NECROLOGY.

Mr. Frank A. Brunner, 910 Filbert Street, Philadelphia, Penna.

LIBRARY NOTES.

RECENT ADDITIONS.

BARROWS, H. K.—Water Power Engineering. 1927.

Chemiker-Kalender: Achtundvierzigster Jahrgang. Three volumes. 1927.

CREAGER, WILLIAM P., and AUSTIN, JOEL D.—Hydro-electric Handbook. 1927.

DAVID, LUDWIG.—Ratgeber im Photographieren. 1927.

EDER, JOSEF MARIA, Editor.—Ausführliches Handbuch der Photographie. Band II, 1 Teil, and Band IV, 2 Teil. Two volumes. 1926–1927.

Elektrotechnischer Anzeiger. Volumes 25, 34–36, inclusive. Ten volumes. 1908–1919.

HILL, E. P.—Rotary Converters: Their Principles, Construction and Operation. 1927.

Institution of Chemical Engineers.—Transactions. Volume 1. 1923.

KETTRIDGE, J. O.—French-English and English-French Dictionary of Technical Terms and Phrases. Two volumes. No date.

MELLOR, J. W.—A Comprehensive Treatise on Inorganic and Theoretical Chemistry. Volume 7. 1927.

Minerva-Index. Geographisches Register zu Minerva Jahrbuch der gelehrten Welt. 28th Jahrgang. 1927.

NEBLETTE, C. B.—Photography: Its Principles and Practice. 1927.

RIDEAL, ERIC K., and TAYLOR, HUGH S.—Catalysis in Theory and Practice. Second edition. 1926.

SEGERBLOM, WILHELM.—Properties of Inorganic Substances. 1927.

STEFFENSEN, J. F.—Interpolation. 1927.

TIEMANN, HARRY DONALD.—The Kiln Drying of Lumber. Third edition. 1920.

TIMOSHENKO, S., and LESSELLS, J. M.—Applied Elasticity. 1925.

UNDERHILL, CHARLES R.—Coils and Magnet Wire. 1925.

BOOK REVIEWS.

QUANTITATIVE ANALYSIS. By Stephen Popoff, Ph.D., University of Iowa. Second edition, xix–559 pages, 68 illustrations, 8vo. Philadelphia, P. Blakiston's Son and Company, 1927. Price, $4.

A comparison of this volume with a copy of Fresenius' manual as used by chemists in the middle years of the last century will show the strides that applied chemistry has made and the direction in which it has gone. The earlier work was a standard for inorganic analysis, and was almost the analysts' Bible. Fresenius' strong leaning towards the purely empirical treatment of analytical problems is said to have been due to his dissatisfaction with the general acceptance by chemists of the unitary system, that is, the system by which, for instance, copper sulphate was written $CuSO_4$ instead of CuO,SO_3. The younger generation of chemists cannot appreciate the bitterness with which this change was met, which included also much antagonism to the doubling of the atomic weights of certain elements such as oxygen and carbon. It is said that when Fresenius found that the unitary formulas were sure to be generally adopted, he abandoned all interest in theoretical chemistry and devoted his energies to the purely practical side. Inorganic quantitative analysis can be carried on without more than a trifling reference to the principles of the science. The results of an analysis of copper sulphate can be checked with equal accuracy by either of the formulas given above. It is worth noting that mineralogists are tending somewhat to use the old-fashioned binary formulas. They find, or think they find, better methods of classifying groups of minerals under that system.

While, as just said, routine mineral analysis may be carried on without reference to theories, progress in the science needs the coöperation of theory. It is not, however, merely the presentation of principles that distinguishes this book from older manuals of quantitative analysis, but the extensive applications of physical chemistry. The books of the last century did not concern themselves with the nature of the atom, the conditions of solutions, the law of chemical equilibrium and the many other data which now figure so conspicuously in works on both pure and applied chemistry. How far an elaborate discussion of these physico-chemical principles will aid the general run of students to develop accuracy in their analytical work may be a question for serious discussion. All teachers have experience of the great inequality of minds of students as far as calculations are concerned. There seems to be in modern works of chemistry an undue tendency to complicate calculations, substituting simple arithmetic by methods of an algebraic nature. It seems, indeed, that the Sörensen scheme of expressing hydrion concentration is unnecessarily complex. A more direct form might have been devised. Some commendable simplifications in spelling, such as "buret" and "pipet," are noted in the book, but the symbol for hydrion concentration is an awkward one, and it is to be regretted that there has not been a general adoption, in this country at least, of the form used by American biologists, pH. Here and there throughout the book, typographic errors are noticeable, among which may be mentioned in the table of contents, "phosphorous" several times.

The book contains a large amount of information on modern methods of inorganic analysis and on the theoretical side with elaborate explanation of the physico-chemical principles applicable to analytical problems.

HENRY LEFFMANN.

MODERN ASTRONOMY: ITS RISE AND PROGRESS. By Hector Macpherson, M.A., Ph.D. vi–196 pages, illustrated, small 8vo. New York, Oxford University Press, American Branch, 1926. Price, $2.

This is a popular treatment of the subject but goes quite comprehensively into the history of astronomy and the development of the modern information and theories. In examining a book of this kind, one turns with some interest to the discussion of Mars which is a sort of storm centre in modern popular astronomy. It is to be regretted that the author has been so enthusiastic in his presentation of what may be called the "Lowellian" views as to Mars. The popular view concerning the possibility of Mars having intelligent beings on its surface seems to be based very largely, as so many other popular views are, upon a mistranslation. When Schiaparelli saw the lines on the Martian surface he called them in his own language "canali" which means "channels." The word was unfortunately translated "canals," and this has come into the English language, apparently permanently, concerning this ruddy-faced planet. "Channels," of course, suggest natural conditions; "canals" carry with them the idea of intelligent purposeful construction. Thus an important point is gained before the general public in developing the notion that Mars contains beings capable of doing work. The phantasy does not stop here. Changes in the tint of the surface are ascribed to the growth and disappearance of vegetation and even some suggestions are made as to the character of this. It is true that the author in speaking of Schiaparelli's work states that the word he used means "channels," but he uses "canals" in all reference to the markings on Mars. Speculation has gone so far as to suggest that there are beings on that planet who are comparable to ourselves and it may be remembered that during the recent near approach to the earth, an American astronomer made the remarkable request that broadcasting should cease for a limited time in order that any message from Mars might be detected. Imagination has no place in scientific work except possibly as a suggestion for research, certainly not in inferential matters. So far as the general text of the book is concerned, it is very readable and doubtless will afford to the unscientific reader considerable entertainment and interest, but it is greatly to be regretted that the interpretations have been so liberal and there has not been more of close scientific criticism presented.

HENRY LEFFMANN.

THE DIAL MACHINE, an apparatus for the elementary mathematical laboratory. By T. C. J. Elliott. 93 pages, 18.4 × 12.7 cm., flexible cloth. Peterborough, The Peterborough Press, 1926. Price, 4/6.

The Dial Machine is a means of illustrating mechanically the idea of functions and variables. The "machine" is rather a system than a definite mechanism. A form which is illustrated consists of a square board upon which are mounted nine dials with graduations. These dials are arranged

in square form in three rows and three columns, and each one is provided with a stationary pointer at which the angular movement may be read. The axles of the dials which pierce the board may be coupled by gearing arranged at the opposite face of the board. The gearing may be covered and made inaccessible to the operator so that the angular movements of the dials may be read without a knowledge of these connections.

The plan of operation contemplated is to tabulate against the motion of a given dial the motions of the others. That is, regarding the motion of the operating dial as the independent variable, to determine the value of the functions from the movements of the others. Many variations may be made including, by the use of epicyclic gearing, functions of more than one variable.

What advantage there is in a device of this kind over representation by coördinated graphs is not apparent. The dial machine can represent only linear functions, while by the common graphic method functions of any character may be represented. The graph method, moreover, can be practically applied to the analysis or design of complex mechanisms by plotting against a common base, which represents the movement of a driving element, the movements of each component operating part. LUCIEN E. PICOLET.

INTERPOLATION. By J. F. Steffensen, Sc.D., Professor of Actuarial Science at the University of Copenhagen. ix–248 pages, 23 × 15 cm., cloth. Baltimore, The Williams and Wilkins Company, 1927. Price, $8.

The process of interpolation by the method of differences as applied to the construction of mathematical tables or to statistical data to which the method is applicable has long been developed into a form suitable for practical use, and adequate texts are available which cover the details of these and other applications. The author of this volume points out that despite those developments a non-rigorous point of view is still dominant in existing texts and that formulas and methods developed on the assumption that the function under consideration is a polynomial are also applied to functions which are not defined. The work of recent investigators, he further states, has developed a number of formulas with remainder terms in a form suitable to the ready determination of the limits of error. The present text, which is based upon lectures of the author to actuarial students at the University of Copenhagen, is in harmony with these recent developments.

The reader is reminded that the work is a text-book and not a reference manual, a fact which becomes apparent upon encountering the subtilities of the operator notation which is employed. The compass of the work is best set forth by an enumeration of the topical headings, which are as follows: Introduction, Displacement-Symbols and Differences, Divided Differences, Interpolation-Formulas, Some Applications, Factorial Coefficients, Numerical Differentiation, Construction of Tables, Inverse Interpolation, Elementary Methods of Summation, Repeated Summation, Laplace's and Gauss's Summation-Formulas, Bernoulli's Polynomials, Euler's Summation-Formula, Lubbock's and Woolhouse's Formulas, Mechanical Quadrature, Numerical Integration of Differential Equations, The Calculus of Symbols, Interpolation with Several Variables, Mechanical Cubature, On Differential Coefficients of Arbitrary Order.

The critical consideration of the remainder term in the development of the formulas and the reduction to a practical form of this term adapted to numerical application in determining the limits of error of a derived value is a unique and valuable feature and in some cases a real necessity. Some twenty pages at the beginning of the work are devoted to an explanation of the special notations adopted and to the demonstration of theorems to be applied in deriving the formulas. Every feature in the derivation of an applicable formula is minutely examined and examples worked out in detail illustrate the conditions under which each should be used. Attention is also given to errors arising from "rounding off" tabular values. In this division, as indeed throughout the work, derivations are made in the most general terms.

The author places a rather high estimate on the analytical capacity of readers of limited mathematical attainment in saying: "The mathematical equipment required in order to master this book is very small." As such things are viewed here, only a reader well trained in analytical operations, and presumably of considerable mathematical attainment, could profitably undertake a perusal of the work. As to the considerable price, a perfunctory examination discloses costly type-setting of a multiplicity of special symbols on nearly every page which, it should be mentioned, constitute an unusually creditable piece of mathematical typography.

This presentation of the subject of interpolation is deductive, rigorous and exhaustive in character, and probably no other text-book in English combines all of these qualities in the degree attained in this one.

LUCIEN E. PICOLET.

INTRODUCTION TO CONTEMPORARY PHYSICS. By Karl K. Darrow, Ph.D. 453 pages, illustrations, 8vo. New York, D. Van Nostrand Company, 1926. Price, $6.

Readers of the *Bell System Technical Journal* have followed with interest the series of articles on "Some Contemporary Physics," by Dr. Karl K. Darrow, member of the Technical Staff.

These articles have now been collected, many of them being recast and expanded into book form and published under the title "Introduction to Contemporary Physics."

The surprising changes that have taken place in physics in the past quarter of a century make this book of especial value in that it brings together, in consecutive and logical order, the phenomena that have been studied and the theories that have been developed to account for them. The discovery of X-rays and radio-activity demand an explanation, and this led to an attack upon the atom, the indivisible unit of Dalton—and this attack resulted in giving us as many complex structures for the atom as there are elements.

The author devotes his first and second chapters to a discussion of the experimental electron and the experimental atom. The "experimental" atom the author defines as the atom found in nature—the atom having measurable qualities of mass, magnetic moment and charge. These are distinct from the various atom-models that have been suggested from the various theories. A similar distinction is made between the electron-model and the "experimental" electron which is discussed in the first chapter.

In the next chapter, which treats of the experimental atom, positive ions, isotopes, the masses of atoms and their magnetic moments are considered. The periodic table of the elements and the service that it has rendered are considered, followed by a discussion of radio-activity.

In a discussion of waves and quanta we are reminded of the contest between the believers in the corpuscular theory upheld by Newton and those who accepted the wave theory of Descartes and Huygens and are told of the experimental verification of that theory by the researches of physicists from Fresnel and Young to Michelson and Rayleigh.

Since the field covered in this book is one in which the phenomena are the results of the activity of the atom and the electron, it was to be expected that attempts would be made to visualize the construction of the atom.

A study of the periodic table with its atomic numbers and of the spectrum of hydrogen resulted in the first of the atom-models, a miniature of the solar system, modified as required by the conditions. How this first model has been changed and the reason for it is clearly described in the parts dealing with Bohr's atom-model for hydrogen and ionized helium and in models for atoms with more than one electron and for molecules.

The purpose of the author in bringing together atomic phenomena, their experimental investigation and their interpretation is a most worthy one, and he deserves great credit for the success of his presentation.

The field covered, though fundamental, is a restricted one, and the reader must not suppose that advances and discoveries in other fields of physics should be overlooked. GEORGE A. HOADLEY.

THE NEW HEAT THEOREM, ITS FOUNDATIONS IN THEORY AND EXPERIMENT. By W. Nernst, Professor at the University of Berlin. Translated from the second German edition by Guy Barr, B.A., D.Sc. xvi–281 pages, 21.5 × 14 cm., cloth. New York, E. P. Dutton and Company, 1926. Price, $4.

The classical thermodynamics of Carnot, William Thomson, Clausius and Rankine contain little reference to other applications than those of power generation and most of the subsequent investigations and writings have been with that end in view. In the course of time the abstract relationships between pressure, volume and temperature which enter into all processes of physical change were applied in the field of chemistry, and modern treatises on theoretical chemistry, such as the "Theoretical Chemistry" of Doctor Nernst, employ these relationships freely, as indeed other dynamical theorems which, only in modern times, have been utilized in formulating the facts of that science. A much broader field for the investigation of the validity of existing laws and new avenues for their extension is thus available to the experimenter.

The New Heat Theorem was first developed and its important applications indicated in a paper published in January, 1906, in the *Nachrichten der Gesellschaft der Wissenschaften zu Göttingen* and later the subject was amplified and appeared in book form. The present volume is translated from the second German edition. The author reviews the fundamental laws of thermodynamics and describes at length the derivation and formulation of the heat theorem. Since its first announcement, much experimental material and theoretical ampli-

fication have become available. All of this is included in the book. The work is an important and possibly an epoch-making contribution to the science of thermodynamics.

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS. Report 248, The Corrosion of Magnesium and of the Magnesium Aluminum Alloys Containing Manganese. By J. A. Boyer. 38 pages, illustrations, quarto. Washington, Government Printing Office, 1926. Price, twenty cents.

Mr. Boyer, Chief Chemist of the American Magnesium Corporation, at the request of the Subcommittee on Materials for Aircraft of the Committee has prepared an exhaustive report on this important subject. The tentative conclusions drawn from the experimental facts of the investigation are as follows:

The over-voltage of pure magnesium is quite high. On immersion in salt water the metal corrodes with the liberation of hydrogen until the film of corrosion product lowers the potential to a critical value. When the potential reaches this value it no longer exceeds the theoretical hydrogen potential plus the over-voltage of the metal. Rapid corrosion consequently ceases. When aluminum is added, especially when in large amounts, the over-voltage is decreased and hydrogen plates out at a much lower potential than with pure magnesium. The addition of a small amount of manganese raises the over-voltage back to practically that of pure metal, and the film is again protective.

Report 250, Description of the N. A. C. A. Universal Test Engine and Some Test Results. By Marsden Ware. 15 pages, illustrations, quarto. Washington, Government Printing Office, 1927. Price, ten cents.

The 5-inch bore by 7-inch stroke single cylinder test engine, used at the Langley Field laboratory of the Committee in laboratory research on internal-combustion engine problems, is described and some results of tests are included.

The engine is arranged for variation over wide ranges, of the compression ratio and lift and timing of both inlet and exhaust valves while the engine is in operation. Provision is also made for the connection of a number of auxiliaries. These features tend to make the engine universal in character, and especially suited for the study of certain problems involving change in compression ratio, valve timing, and lift.

Incidental to investigations of carburetor and fuel injection engine problems considerable data have been obtained which indicate the effect of changes of compression ratio on friction horsepower and volumetric efficiency. From this and some other work, it appears that with a change in compression ratio from 5 to 13, the friction horsepower obtained by motoring the engine increases by about 15 per cent. The volumetric efficiency of the engine was found to remain practically unchanged between compression ratios of 5.3 and 7.3 with carburetor operation and between 9.5 and 13 with fuel-injection operation.

The results of some tests are presented also that show the power obtained when operating as a carburetor engine on aviation gasoline at compression ratios in excess of that which will permit full throttle as a normal engine and controlling detonation by throttling the intake charge and by varying the inlet valve timing. For fixed compression ratios in these tests throttling gave the least power while variation of the inlet valve closing time with the opening time kept fixed gave the greatest power for the conditions tried.

Report 255, Pressure Distribution over Airfoils at High Speeds. By H. L. Briggs and H. L. Dryden. 42 pages, illustrations, quarto. Washington, Government Printing Office, 1927. Price, fifteen cents.

This report deals with the pressure distribution over airfoils at high speeds, and describes an extension of an investigation of the aerodynamic characteristics of certain airfoils which was presented in N. A. C. A. Technical Report No. 207. The work was carried out at the request and with the financial assistance of the committee. A large compressor plant at Edgewood Arsenal was made available for the experiments through the courtesy of the Chemical Warfare service.

The results presented in Report No. 207 have been confirmed and extended to higher speeds through a more extensive and systematic series of tests. Observations were also made of the air-flow near the surface of the airfoils and the large changes in lift coefficients were shown to be associated with a sudden breaking away of the flow from the upper surface.

The tests were made on models of 1-inch chord and comparison with the earlier measurements on models of 3-inch chord shows that the sudden change in the lift coefficient is due to compressibility and not to a change in the Reynolds Number. The Reynolds Number still has a large effect, however, on the drag coefficient.

The pressure distribution observations furnish the propeller designer with data on the load distribution at high speeds, and also give a better picture of the air-flow changes.

PUBLICATIONS RECEIVED.

Pharmaceutical and Medical Chemistry, by Samuel P. Sadtler, Ph.D., Virgil Coblentz, Ph.D., and Jeannot Hostman, Ph.G. Sixth edition revised and rewrittten by Freeman P. Stroup, Ph.M. 748 pages, illustrations, 8vo. Philadelphia, J. B. Lippincott Company, 1927. Price, $7.

Quantitative Analysis, containing Theory and Practice of Modern Analytical Chemistry with Problems and Explanations of Calculations, by Stephen Popoff, Ph.D. Second edition. 559 pages, illustrations, 8vo. Philadelphia, P. Blakiston's Son and Company, 1927. Price, $4.

Equilibria in Saturated Salt Solutions. A summary of the results of the study of the heterogeneous equilibria which exist in aqueous solutions of electrolytes, by Walter Charles Blasdale. American Chemical Society Monograph Series. 197 pages, illustrations, 8vo. New York, The Chemical Catalog Company, Inc., 1927. Price, $4.50.

Properties and Testing of Magnetic Materials, by Thomas Spooner. 385 pages, illustrations, 8vo. New York, McGraw-Hill Company, Inc., 1927. Price, $5.

Modern Astronomy: Its Rise and Progress, by Hector Macpherson, Ph.D. 196 pages, illustrations, plates, 12mo. New York, Oxford University Press, 1926. Price, $2.

Marvels of Modern Mechanics. The mastery of land, sea and air, by Harold T. Wilkins. 280 pages, illustrations, plates, 12mo. New York, E. P. Dutton and Company, 1927. Price, $3.

National Advisory Committee for Aeronautics. Technical Notes, No. 255, Precision of Wing Sections and Consequent Aerodynamic Effects, by Frank Rizzo. 11 pages, illustrations, photograph, quarto. Washington, Committee, 1927.

Volumetric Determination of Cuprous Oxide.—CHARLES S. BISSON and J. GORDON SEWELL, of the University of California (*Jour. Asso. Official Agric. Chem.*, 1927, **10**, 120–124), have devised a new procedure for the volumetric determination of the cuprous oxide which is precipitated by reducing sugars. The cuprous oxide is collected on an asbestos filter, then treated with an excess of a standard solution of potassium permanganate in the presence of sulphuric acid. An excess of a standard solution of ferrous sulphate is next added. The resulting solution is titrated with the standard solution of potassium permanganate to the usual pink end point. However, if sufficient copper be present to impart a blue color to the solution, then the end point is a change from blue to lavender. Knowing the total volume of standard potassium permanganate solution and of standard ferrous sulphate solution used, the mass of cuprous oxide is readily calculated. J. S. H.

Pilot Balloons Supply Upper-air Wind Data. (U. S. Department of Agriculture, Press Service, Clip Sheet No. 454.)—The work of the Weather Bureau in studying upper-air conditions by means of pilot balloons has recently been compiled in the form of an aerological survey of the United States for the benefit of aviators. The direction and velocity of the winds at different flying levels have been carefully studied and tabulated in such form that any given region can be studied separately. In general, it has been found that surface velocities differ little with season, latitude, or wind direction. From the surface to about 500 metres elevation winds of all directions usually veer and increase in velocity, these tendencies being most pronounced with southerly winds. The terms southerly, westerly, easterly, and northerly are understood to mean coming from those directions. At higher levels velocities continue to increase above westerly winds, but they often decrease slightly above easterly winds. These changes are accompanied by continued veering above southerly winds, but by a backing or reversing above northerly winds, the result being a fairly close approach to a westerly direction, except that winds above northeast to east surface winds are very irregular. The changes with season and latitude, small at the surface, increase decidedly with altitude. In general, the highest velocities and the nearest approach to a westerly direction occur when and where the poleward temperature gradient (change with latitude from warm in the south to cold in the north) and therefore the poleward pressure gradient (change in pressure from high in the south to low in the north) are most marked —that is to say, in winter and in the northern part of the country.

CURRENT TOPICS.

Meteorological Conditions and Sound Transmission. E. S. PLAYER. (*Quarterly J. Roy. Meteorological Soc.*, Oct., 1926.)—As long as mankind continues to rely upon information received by sounds that have come long distances so long will the conditions that modify audibility receive attention both for their scientific interest and for their practical importance. In the years 1921–1922 a series of experiments on this subject was conducted off the coast of England by Mr. Player, who is a technical assistant in the Acoustical Section of the Air Defence Experimental Establishment. Like his predecessor in this type of investigation, John Tyndall, he was assisted by the Elder Brethren of Trinity House, who control the coast lights of the country. The source of sound was a siren on the North Goodwin light-vessel a few miles from the North Foreland, the point in Kent farthest to the east and on the south side of the Thames estuary. The pitch of the siren was practically constant at 180 vibrations per second. At the observing station measurements were obtained by the record of deflections of "a galvanometer connected to a Wheatstone bridge, one arm of the latter being formed by a doubly-resonated hot-wire microphone, which acted as a receiver."

As proof of the rapidity with which acoustical conditions changed with consequent variation in the loudness of the sound heard a series of galvanometer deflections caused by blasts from the siren at intervals of one minute may be cited. The first deflection was 1; the second, a minute later, was 4; the third, 1; the fourth, 0. In one case a deflection of 6 is preceded by two readings of 1 and followed by three of 1. The most irregular succession is 1, 0, 8, 1, 1. The experiments were ended by the siren becoming inaudible and remaining so for half an hour. As a wind was blowing the variations in the strength of the signals was at first ascribed to it, but on a later day there was an even more pronounced difference, though only a light wind prevailed. It seemed therefore that the cause of variability must be sought in changes of physical variables other than wind velocity. A curve is given showing close correlation between audibility and humidity. They rise and fall together. "The writer watched the pen (of the hygrograph) falling, while listening at the same time to the sound dying down to inaudibility." The effects of rain were by no means consistent. "Sometimes when the siren was blowing, but inaudible, it would become audible during a period of rain and die out again when the rain stopped; on the other occasions the exact opposite was the case." For sounds starting from sources close to the surface of the earth audibility was worst on "oppressive" days, when the air was quiet, the sky cloudless, shade temperatures high and temperatures in sunlight low, with a haze dimming the sun.

The results given above held for sounds travelling in a general horizontal direction. Another set of observations was made on the sounds originating in an airplane flown after sunset. Such sounds came down in a roughly vertical direction through air in which the arrangement of physical properties is different from that in a horizontal path. "The range of audible transmission was good on every occasion that the general humidity of the atmosphere at all levels was high, and usually, but not always, poor when it was low." This is attributed to the close association of high humidity with homogeneity of the atmosphere. The only meteorological factor that varies with a rapidity equal to the rate at which audibility changes is humidity. The author adduces an instance when in 4½ minutes a hygrograph showed a change in relative humidity of 15 per cent., there being meanwhile no change of temperature or of other conditions.

In this paper the effect of change of temperature receives less consideration than would be expected. In one airplane flight there were parts of its course from which the sound was audible.

After the reading of this communication before the Royal Meteorological Society the discussion that followed brought out some interesting facts. Mr. Bonacina stated that in Essex during the war the sound of gun fire at a long distance would be heard only from May to August, while in some other parts of Europe audibility was confined to the winter months. He had noticed that firing was heard more distinctly inside a wood than outside it. G. F. S.

On the Densities of Particles in Smoke. H. S. PATTERSON and R. W. GRAY. (*Proc. Royal Soc.*, A764.)—If the size of small particles is to be determined by their rate of fall in air or other gas, a knowledge of their density is needed. This is often taken to be the same as that of the substance in large quantities—an assumption probably correct for liquids and for solids in certain cases but not true for solid particles with a loose structure. Such a structure has been shown to exist for large particles in the cases of smokes made up of the oxides of cadmium, zinc and magnesium. "Further, it seems probable that the smaller particles of so-called ultra-microscopic size in these smokes also possess a similar structure, since they are formed in the same way and consist most likely of a number of primaries."

In what follows the "density of a particle" means the density of a sphere of the same mass as the particle, which falls through air at the same rate as the particle. If the particle be composed of several parts irregularly grouped, the density as just defined would be expected to be less than that of a homogeneous sphere of the substance. Consider, for example, a gram of glass wool. Let the time be found that it takes it to fall 10 feet. Melt the wool into a single sphere of glass. This will fall through the 10 feet in a less time than the wool, though its mass is the same. Thus to get a sphere of the same mass and the same time of fall, its density must

be reduced. Kohlschutter and Tuscher, working with electrically precipitated smokes, found their densities to be much less than that of the normal substance. The smoke of aluminium oxide, as an example, had only 5 per cent. of the density of the oxide in bulk. They further found that the density of smokes of the same substance varied greatly according to the method of production.

The author attacks the problem of the density of smoke particles by the use of the method Millikan applied so successfully to the determination of unit electronic charges. The motion of smoke particles was observed while they were acted on by a vertical electrostatic field as well as by gravity, or by the latter alone. Their electrical charges were varied by bringing radium near. From the data thus obtained the density can be calculated. "Cadmium oxide, silver and gold were produced by making an arc between poles of the various metals in a cubic metre chamber. Magnesium oxide was made by burning magnesium ribbon, and mercuric chloride and mercury by volatilization from an electrically heated boat." The calculated densities are remarkably small. For gold smokes they range from 8.0 to .21, though gold itself has the value 19.3. In the case of cadmium oxide the smallest density was for a particle that was seen to consist of a chain of parts. "The simplest interpretation of the results is to assume that the smoke particles are loosely packed aggregates, made of primaries, which are in many cases ultra-microscopic." An additional conclusion is reached, that smoke particles are in reality considerably larger than has been supposed, indeed often being of microscopic and not of ultra-microscopic dimensions. This was confirmed by microscopic examination of the particles that settled upon slides. Their complex chain or ring structure was often visible. G. F. S.

The Thermal Conductivity of Vitreous Silica. G. W. C. KAYE and W. F. HIGGINS. (*Proc. Royal Soc.*, A764.)—While vitreous silica is growing more important, but little is known of its thermal conductivity. Eucken and Barratt both have determined it but their results are not in agreement. For instance, at 100° Eucken's value is nearly twice that of Barratt.

The method employed in this investigation is that of the "divided bar," due to Sir Oliver Lodge in 1878. "A bar of metal heated at one end and cooled at the other is divided by a plane perpendicular to its axis, and a plate of the material under test is interposed. It follows that, under steady conditions of heat flow, the ratio of the conductivities of the specimen and of the bar is equal to the inverse ratio of the temperature gradients in the specimen and in the bar immediately adjacent to the specimen." Aluminum bars were used on account of the high conductivity of this metal and of its freedom from oxidation. Since the divided bar method gives only a ratio, it was necessary to measure the conductivity of aluminum. The published values for this quantity differ by as much as 14 per cent. The

numerical value of the thermal conductivity was found to be .54 in c.g.s. units with an increase in the third decimal place of one unit for each 50° C. increase from 50° to 250° C.

The divided aluminum bar was 14 in. long and, after it had been cut into two pieces 7½ and 6½ in. long, the cut surfaces were made optically flat and polished, thus securing good thermal contact with the similarly treated surfaces of silica. The lengths of the three specimens of silica used were 1, 1.5 and 2 mm., respectively. Thermocouples were used to measure temperatures. The apparatus was put in a thermostatic enclosure so that the mean temperature could be varied and the conductivity determined at different temperatures. This was found to be, in c.g.s. units, .0033 at 60° and .0036 at 240° C. Further measurements were made with plates of natural quartz 1/10 in. thick. When the heat flowed parallel to the optical axis the conductivity fell from .0222 to .0186 when the temperature rose from 68.1 to 104.3°. With the heat flowing perpendicular to the axis a rise of temperature from 70.4° to 105.5° causes the coefficient to decrease from .0129 to .0116. It is thus seen that amorphous vitreous silica has a much greater conductivity than quartz and that an elevation of temperature increases the conductivity of silica but reduces that of quartz. G. F. S.

Experimental Contributions to the Theory of the Process of Diffusion. E. WILKE and W. STRATHMEYER. (*Zeit. f. Physik*, **40**, Nos. 1 and 2.)—Since Fick in 1855 gave to the law of diffusion its classical form, experiments in this field have not lacked. One result has been to show that the constant of diffusion of Fick's formula is in reality no constant but a variable depending upon the concentration of the solution in question. The methods early used to study diffusion depended upon determining the concentration at different levels by finding the quantity of diffusing substance in a somewhat extended volume. Such methods were not fine enough to reveal the connection between concentration and coefficient. The optical method of Otto Wiener made this possible, yet even this was not adequate to the study of a relation between the coefficient and the gradient of diffusion. The need was for a method of learning the concentration at any instant and at any point in the solution. The author believes he has found a way of doing this by the use of little floats of capillary glass tubing. They are 1 mm. in diameter and about 2 cm. long, and they must float horizontally in a liquid of uniform density. Such floats cannot be made according to specifications. Five thousand were made and from these were selected those that combined a proper specific gravity with the quality of floating in the position desired. "The accuracy of the measurement of concentration by this means is extraordinarily great." The position of a float is readily determined to .1 mm. It was found that the distance traversed by a float under the influence of diffusion was affected by the occurrence of slight vibrations in the vessel. As would be expected, slight changes of tem-

perature are even more effective in disturbing the orderly progress of diffusion. For example, a lamp held for a few seconds near one end of a float makes it take a slanting position. Similarly the heat from the observer's body produces the same effect.

Three acids were studied, HCl, HI and HBr. For all three the coefficient increases with the concentration. In the case of HI its value is four times as great when the specific gravity is 1.59 as when it is 1.014. Furthermore there seem to be two maximum values of the coefficient at concentrations twice and fourfold normal. Another regularity showed itself in this, that in general the coefficient for any concentration grew larger with the progress of time. G. F. S.

The Measurement of Transmission and Reflection of Sound by Partitions of Felt. A. H. DAVIS and T. S. LITTLER. (*Phil. Mag.*, Jan., 1927.)—Sound may pass from one side of a partition to another in at least three ways. The waves may find a path through openings or holes. They may set up longitudinal vibrations in the partition which, having traversed its thickness, causes waves in the air on the distant side, or the partition may be made to vibrate as a whole, the air beyond it being caused to vibrate by its motion. The last method seems the most important in the transmission of sound through solid partitions.

W. C. Sabine gave a method for measuring the transmission of sound through a substance. Sheets of the material were placed across an opening joining two adjacent rooms. A sound was produced in one and the duration of its audibility after cessation was measured in both of them. "Unfortunately, the method requires very large rooms and would usually involve the erection of a special building." F. R. Watson, of the University of Illinois, devised a less expensive plan of measurement, which the author employed in his experiments. The test material in sheets 5 ft. × 4 ft. was fixed across an opening between two sound-proof rooms where ceiling, floor and walls were covered with absorbing material. Waves from an electrical loud-speaker were directed by a paraboloid mirror upon the sheets. Absorbing screens were located in both rooms where their presence would reduce the intensity of the sound reflected and avoid the formation of stationary waves. A telephonic device was used to measure the sound transmitted. It was proved by examination that merely putting the sheets into position did not change the performance of the source of sound. Measurements were made of the intensity of sound in the beam reflected back into the room where the loud-speaker was located and also of the intensity in the transmitted beam. "In the reflection room the general intensity in positions screened from direct radiation from the loud-speaker is only about 0.13 per cent. to 4 per cent. of the intensity in the transmitted beam." With a frequency of 2000 it made considerable difference in the reflected sound whether the test material across the opening was stretched

smoothly or not. With 700 vibrations per second, the difference became negligible.

Of the substances tested a blanket turned out to be the best transmitter of sound while its reflecting power was small. Felt transmitted only 21 per cent. as large a part of the incident pressure-amplitude as did the blanket, but it reflected nine times as much. Hair-felt in thicknesses of one, two, three and four layers was used across the opening. For frequencies ranging from 250 to 1600 one layer transmitted about .3 of the energy falling on it, but when more layers were applied, the ratio of transmission varied considerably with the pitch of the sound. For example, with a frequency of 1600 four layers transmitted .002 of the incident energy, while they transmitted .04, twenty times as much, of the energy falling on them, the frequency being 250. G. F. S.

Philosophical Apparatus of Joseph Priestley.—C. A. BROWNE (*Jour. Chem. Ed.*, 1927, **4**, 184–199) describes the apparatus used by Joseph Priestley during his life in America and still in existence. The major portion is in the Priestley Museum at his old home at Northumberland, Penna. His apparatus, formerly exhibited in the U. S. National Museum, has been deposited at Northumberland as an indefinite loan. Certain pieces of his apparatus are in the possession of Dickinson College at Carlisle, Penna.; and his air-pump is the property of The Franklin Institute. J. S. H.

The Measurement of Air Quantities and Energy Losses in Mine Entries. A. C. CALLEN and C. M. SMITH. (Bulletin No. 158, Engineering Experiment Station of the University of Illinois.)—The importance of ventilation in coal mines with respect to safety cannot be over-emphasized. With the increase in the size of modern mines and the very gassy condition of some of them the problem of handling large volumes of air in the mine so as to have efficient and safe ventilation at reasonable cost becomes increasingly difficult.

Very little work has been done in determining the laws governing the flow of air in mines. The Atkinson formula, $R = ksv^2$, proposed in 1854, stating that the mine resistance, or the total resistance to flow, varies directly as the rubbing surface and the square of the velocity, has been considered satisfactory for most uses.

Within the last three or four years the United States Bureau of Mines has carried on some investigations on this subject and important information has been obtained regarding coefficients of friction and certain features of air-flow. The quantity of air was measured by pitot-tube traversing at a specially-constructed air-measuring station and a study of the results obtained indicates a high degree of accuracy.

Since the building of special air-measuring stations at operating mines involves considerable expense, the primary object of the investigation was to see whether pitot-tube traversing methods could be

applied with reasonable accuracy at any desired location without building a measuring station and without special preparation of the section. As a secondary feature it was planned to secure pressure-loss data in conjunction with the velocity measurements in order to obtain information on the magnitude of the so-called "friction" losses, as well as of the losses due to splitting, special resistances, etc.

Among the conclusions drawn were the following:

(1) It is possible to measure air quantities in coal-mine airways by pitot-tube traversing methods and to obtain check results that are reasonably accurate when it is remembered that the quantity of air flowing in a mine airway is a varying quantity, being affected by a number of mine activities.

(2) While check results can be secured by anemometer traversing yet the values thus obtained are much higher than the true quantities. It seems improbable that anemometer determination can be relied on unless the anemometer is calibrated under the exact conditions of use.

(3) The effect of the disturbances on ventilation produced by the normal operating activities of the mine is very marked. Not only are there appreciable changes in quantity but the pressure losses show great fluctuations due to the changes in the circulation of the air caused by opening and closing of doors and by trips of cars obstructing the entries.

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